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THE KINETICS OF THE OLEFINE-BROMINE REACTION

Part IV. The Rate Equation of the Homogeneous Catalysed Thermal Reaction

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Received March 7, 1946

A tentative mechanism for this reaction was proposed by the author[1] and this was subsequently modified[2] so as to bring the thermal mechanism in line with the photochemical change. Since then, further work has shown that an examination of the results with a suitable reaction rate equation based on the mechanism is necessary and this constitutes the subject of the present communication.

A homogeneous catalysed reaction such as the ones under consideration can involve activation of one or both of the reactants by the catalyst. Any derivation of the kinetic equation has to consider both alternatives. The process of activation may involve the communication of the activation energy effectively to the molecules that would otherwise acquire it only very slowly and the molecules thus activated may react only after some interval during which they are liable to deactivation. As postulated in the tentative mechanism, the catalyst may remain associated with the reactant as a complex which undergoes the reaction. The various processes taking place and the concentrations involved are collected in Table I.

Table I

Process	Concentration	Rate Constant
Activation of reactant 1 ..	n_1	k_1
Deactivation of activated reactant 1 ..	a_1	k_2
Activation of reactant 2 ..	n_2	k_3
Deactivation of activated reactant 2 ..	a_2	k_4
Reaction between the activated reactants ..	a_1, a_2	k_5

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If the concentration of the catalyst is c, we get for the stationary concentration of the activated molecules the relation:

$$k_1 n_1 c - k_5 a_1 a_2 - k_2 a_1 c = 0$$

$$k_3 n_2 c - k_5 a_1 a_2 - k_4 a_2 c = 0.$$

From these two simultaneous equations, one gets

$$a_1^2 + a_1 (k_1/k_2 \cdot n_1 - k_4/k_5) - (k_1/k_2 \cdot k_4/k_5 n_1 c) - (k_3/k_2 n_2) = 0$$

Neglecting the last term which involves neither the catalyst nor the reactant 1 and taking only the positive root of the quadratic for a_1, the reaction velocity equation

$$dx/dt = k_5 a_1 a_2$$

becomes

$$dx/dt = k_1 k_3 k_5 \, n_1 n_2 c / k_2 k_4 c + k_1 k_5 n_1.$$

Applying this to the Olefine-Bromine reaction catalysed by hydrogen bromide we have

$$dx/dt = k_1 k_3 k_5 \, [\text{Olefine}] \, [\text{Bromine}] \, \frac{[\text{Hydrogen Bromide}]}{k_2 k_4 \, [\text{HBr}] + k_1 k_5 \, [\text{Br}_2]} \qquad (1)$$

If one considers, however, that only one reactant gets activated by the catalyst, we get for the stationary state

$$k_1 n_1 c - k_2 a_1 c - k_5 a_1 n_2 = 0$$

and

$$dx/dt = k_5 a_1 n_2 + k_5 k_1 n_1 n_2 c / k_2 c + k_5 n_2.$$

This gives for the present reaction

$$dx/dt = k_5 k_1 \, [\text{Olefine}] \, [\text{Bromine}] \, [\text{Hydrogen Bromide}] / k_2 \, [\text{HBr}] \, k_5 \, [\text{Olefine}] \qquad (2)$$

Expressing the hydrogen bromide concentration as a molefraction of the bromine concentration, f, equations 1 and 2 may be rewritten

$$dx/dt = k_1 k_3 k_5 \, [\text{Olefine}] \, [\text{Bromine}] \, \frac{f}{k_2 k_4 f + k_1 k_5} \qquad (3)$$

$$dx/dt = k_1 k_5 \, [\text{Olefine}] \, [\text{Bromine}] \, \frac{f}{k_2 f + k_5} \, [\text{Olefine}]/[\text{Bromine}] \qquad (4)$$

If olefine and bromine concentrations are chosen to be equal and the coefficients of f be unity, both expressions lead to an identical one of the type

$$dx/dt = k' \, [\text{Olefine}] \, [\text{Bromine}] \, \frac{f}{f + 1}. \qquad (5)$$

Obviously this assumption cannot be valid in all cases but one may expect that in every instance, a range of catalyst concentration may be found where this holds good. Further, the expression will be reduced to a simple

bimolecular type if $f = \frac{k_1 k_5}{k_1 k_5 - k_2 k_4}$ in equation (3). Equation (4) will be similarly reduced to this type if the reactants are initially at the same concentration and $f = 1/1 - k_2/k_5$. It has been observed that the introduction of activating groups reduces both the period of induction and influence of the catalyst on the rate of the addition reaction ( ). One may expect, therefore, for each olefine three different stages in the catalysed reaction:

1. The reaction is represented by the full rate equation (3).
2. The reaction is represented by the rate equation (5).
3. The reaction gives a bimolecular constant.

Evaluation of all the constants in the full rate equation is not feasible with the existing experimental data but the general validity of the concepts may be seen by examining the figures for crotonic acid (Tables II, III and IV).

The three tables present data which correspond to the different stages mentioned in the foregoing para in the order given. The experimental work in the earlier parts of this work has shown that though the determining factor

TABLE II

Concentration of Olefine = Concentration of Bromine M/15 ; Concentration of Catalyst (HBr) : 1·05 moles % of Br

Reaction %	Rate Constant mole/min.$^{-1}$ calculated using Eqn. 5	Rate Constant mole/min^{-1}. Bimolecular
10	2·006	0·0168
15	2·395	0·0195
20	2·865	0·0221
25	3·115	0·0238

TABLE III

Concentration of Olefine = Concentration of Bromine M/15 ; Concentration of Catalyst (HBr) : 2·10 moles % of Br

Reaction %	Rate Constant using Equation 5 moles/min.$^{-1}$	Rate Constant, Bimolecular moles/min.$^{-1}$
10	1·31	0·0192
15	1·37	0·0228
20	1·35	0·0250
25	1·34	0·0269

TABLE IV

Concentration of Olefine = Concentration of Bromine M/15; Concentration of Catalyst, (HBr) : 6 90 moles % Br

Reaction %	Rate Constant using Equation 5 moles/min.$^{-1}$	Rate Constant, Bimolecular moles/min.$^{-1}$
10	1·267	0·0538
15	1·340	0·0552
20	1·422	0·0552
25	1·485	0·0554

Note.—The rate constants in Tables II, III, IV refer to a temperature of 35.5° C.

in the reaction is the ratio between the catalyst and bromine, the dual activation of the double bond, *viz.*, the internal group influences and the external catalyst influence, has to be recognised and though equation 5 and the bimolecular equation can both be derived from the simpler set of reaction the more complete one is to be preferred.

Since in every case the limiting reaction is a bimolecular one,* the limiting value of the velocity constant will be proportional to $\frac{k_1k_3}{k_1k_3 - k_2k_4}$. Each of these constants being specific for a reaction different catalysts may be expected to lead to different limiting values of the velocity constant. Also, the catalyst-bromine concentration ratio for each of the stages may not be the same. The following data obtained with iodine monochloride as catalyst and crotonic acid as the olefine illustrate this point.

TABLE V

Olefine and Bromine concentrations M/15

Catalyst Concentration	Reaction %	Rate Constant Eqn. 5	Rate Constant, Bimolecular
0·95 % Bromine	10	2·497	0·0109
	15	2·891	0·0228
	20	2·981	0·0252
	25	3·134	0·0296
7·80 % Bromine	10	0·8005	0·0521
	15	0·6861	0·0541
	20	0·6434	0·0552
	25	0·5659	0·0545

* Note Robertson and co-workers (*J.C.S.*, 1945, 129 &c.) at higher concentrations get the reaction as termolecular. This is considered in a later part.

The applicability of the equation to other compounds and the influence of substituent groups are considered in the next part.

Summary

A kinetic equation has been derived for a homogeneous catalysed reaction in which both the reactants of a bimolecular reaction are activated by the catalyst and the equation applied to the reaction between crotonic acid and bromine catalysed by hydrogen bromide. The variation of rate with change of catalyst is also indicated.

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THE KINETICS OF THE OLEFINE-BROMINE REACTION

Part V. Influence of Substituents on the Applicability of the Kinetic Equation of the Catalysed Reaction

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In Part I of this series it was observed that the induction period and the minimum concentration of catalyst needed to eliminate this varied with the olefine and a hypothetical curve was drawn correlating these.[3] The kinetic equation derived in Part IV (preceding paper) must be consistent with this observation if it is to be a general one. Two similarly substituted trans ethylene derivatives were chosen for this study, fumaric acid and stilbene. The choice of these was determined by the following considerations: In dealing with a reaction involving the polarisability of the double bond, the complication of dipole moment influence has to be minimised and symmetrically substituted trans compounds present the obvious choice. An increase in the number of activating groups attached to the doubly bound carbon leads to a very fast reaction which renders accurate experimental work difficult with available equipment. Alpha-beta unsaturated acids have been shown by Kharasch[8] to be free from the complication of a peroxide effect. Phenyl ethylene reacts faster than ethylene but one may expect the symmetrical diphenyl ethylene to be less reactive through the opposing influences of the phenyl groups. The deactivation, however, cannot be as great as with the two carboxyl groups. Combining with the earlier observations, it was expected that a more exact correlation between activation and catalytic influence could be obtained. The results of the kinetic investigations are given below (Figs. 1 and 2) (Tables I, II, III, IV, V and VI).

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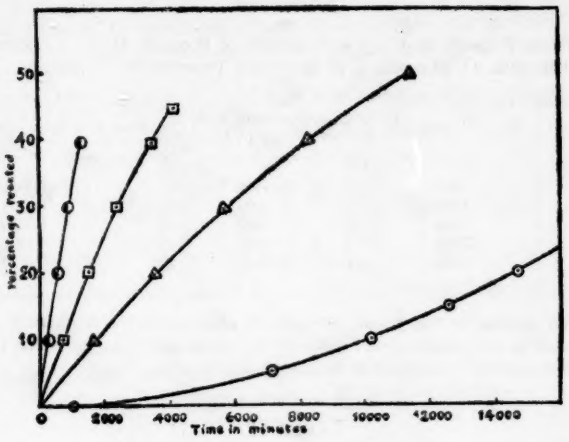

FIG. 1.

I. Uncatalyed Reaction.
II, III, IV. Catalysed reactions at 35°.5 C., 43°.5 C. and 50°·6 C.

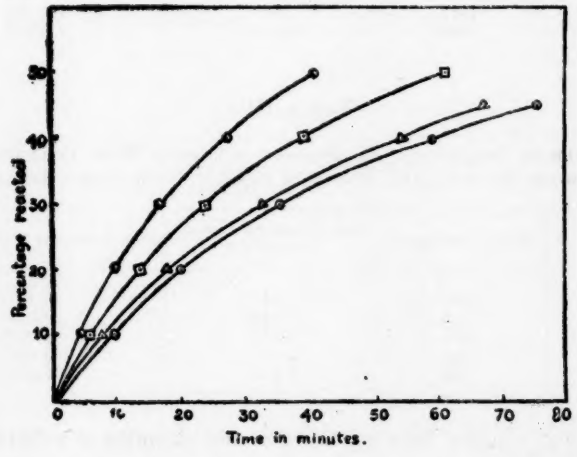

FIG. 2

I. Uncatalysed Reaction.
II, III, IV. Catalysed reactions at 35°.5 C., 43° C. and 50°·55 C.

TABLE I

Concentration of Fumaric acid* ; Concentration of Bromine M/30 ; Concentration of Hydrogen Bromide 11·01 moles % of Bromine ; Temperature of reaction : 35°·5 C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	852	0·0189	0·00185
10	1698	0·0194	0·00196
15	2604	0·0193	0·00203
20	3576	0·0194	0·00210
25	4596	0·0191	0·00217

* *Note.*—After writing up this paper, the authors came across the work of P. W. Robertson *et al.* in which fumaric acid happens to be one of the compounds studied. The bearing of that on the present work will be considered in a later communication.

TABLE II

Concentration of Fumaric acid ; Concentration of Bromine M/30 ; Concentration of Hydrogen Bromide 11·01 moles % of Bromine ; Temperature of reaction : 43° C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	344	0·0450	0·00459
10	712	0·0450	0·00468
15	1100	0·0453	0·00481
20	1512	0·0453	0·00495
25	1956	0·0452	0·00512

TABLE III

Concentration of Fumaric acid ; Concentration of Bromine M/30 ; Concentration of Hydrogen Bromide 11·01 moles % of Bromine ; Temperature : 50°·6 C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	134	0·117	0·0118
10	274	0·116	0·0122
15	427	0·112	0·0124
20	598	0·107	0·0125
25	790	0·109	0·0127

The thermal reaction between Stilbene and Bromine is a fast one and it was found that a concentration of M/30 the reaction was completed in less than half an hour. To bring the speed of the reaction within measurable control, it was found necessary to work with concentrations of M/600.

TABLE IV

Concentration of Trans-Stilbene ; Concentration of Bromine M/600 ; Concentration o. Hydrogen Bromide 11·01 moles % Bromine ; Temperature 35°·5 C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	3·8	8·12	8·21
10	7·9	7·74	8·44
15	12·6	6·91	8·40
20	18·4	6·36	8·15
25	24·8	5·84	8·06
30	32·7	..	7·87

TABLE V

Concentration of Stilbene ; Concentration of Bromine M/600 ; Concentration of Hydrogen Bromide 11·01 % of Bromine

Temperature	43°·0 C.		50°·55 C.	
Reaction %	Time in minutes	Rate Constant " Bimolecular "	Time in minutes	Rate Constant " Bimolecular "
5	2·9	10·89	2·1	15·04
10	6·1	10·93	4·35	15·33
15	9·7	10·89	6·95	15·24
20	13·9	10·79	9·95	15·08
25	18·5	10·81	13·10	15·26
30	23·8	10·80	16·95	15·17

TABLE VI

(All values refer to 35°·5 C.)

Reacting Olefine	Concentration Moles/litre	Induction Period in minutes	" Velocity Constant " mol./litre, min.$^{-1}$
Crotonic acid ..	M/30	25	0·038
Tiglic acid ..	'	4	0·20
Dimethylacrylic acid ..	'	1·2	0·78
Fumaric acid ..	,,	1062·0	0·0020
Allyl Chloride ..	M/300	Less than 2	1·22
,, Bromide ..	,,	2·5	0·72
Stilbene ..	,,	Ca 3·8	0·40 (estimated) by extrapolation

It will be noticed that fumaric acid gives a reasonable " bimolecular " constant only at about 50° C. even though the proportion of catalyst is the same as that used in earlier experiments. On the other hand, stilbene at 35·5 can be considered to behave equally well by the use of Equation 5 or

the bimolecular rate equation and at higher temperatures gives a good bimolecular constant. Qualitatively, therefore, one may conclude that the minimum concentration of the catalyst required for giving a " bimolecular " constant is greater in the case of an olefine with deactivating groups than that of one with activating groups, the limiting value being reached earlier in the latter case.

To get a better picture of the role of activating groups, one can compare the limiting value of the constants where possible with the induction periods observed or what probably amounts to the same thing, with the minimum concentration of catalyst required to give a bimolecular constant.

If one were to plot the values of the " velocity constant " at comparable concentrations against the induction periods, a curve asymptotic towards both axes can be obtained but the experimental values for the purpose has still to be obtained. The figures in the table (Table VI), however, clearly show the trend expected.

One may then justifiably cousider that the rate equation derived in the previous part (IV) fits in with the behaviour of both structural influences and catalytic influences.

In Part I of this series[2] it was observed that the experimental observations of Williams[7] on the addition of bromine to ethylene in carbon tetrachloride solution showed the characteristics of a chain reaction and that the per cent. reaction-time curve could be represented by the relation of the type:

$$x = \frac{100}{1 + e^{-\phi\theta}}.$$

It was anticipated then that in the non-polar solvent there is a likelihood of a heterogeneous reaction complicating the interpretation. The recent observations of Robertson and co-workers appears to indicate the presence of a definite heterogeneous reaction in this solvent. All observations in acetic acid, however, indicate that the reaction in this polar solvent is definitely homogeneous. While the polar solvent can function as an activating medium for the reaction, in the case of olefines where deactivating groups are present and where the concentration of the added external catalyst is not adequate, the competition between the acetanion and the bromide ion in the latter steps in the reaction may slow down the rate and the reaction-time curve stmulates one of a degenerate branching chain. This anticipation is borne out by the uncatalysed addition to fumaric acid at 35° C. (Fig. 3).

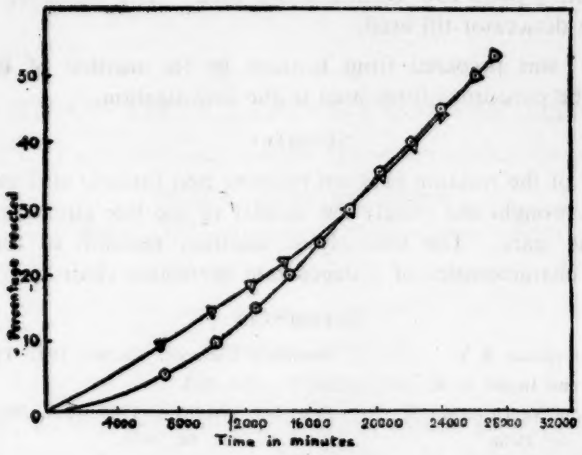

FIG. 3

I. Theoretical, II. Experimental.

Strict conformity between the theoretical and experimental values may not be expected in the initial stages of chain development but the coincidence is nonetheless striking. The maximum value of the reaction rate is reached when about 50% of the reaction is over, again, conforming to Semenoff's generalisations on degenerate branching chains.[6] It is expected that further work in progress will reveal other similar instances.

A word of explanation is necessary for the choice of an aryl ethylene in the investigation. Competition experiments had shown[2] that the introduction of the phenyl nucleus activates the double bond. From the genesis of the T-effect, that the location of two groups of this class of substituents may be expected to neutralise each other's influence, especially if the trans form were chosen. Unpublished observations of one of us in the competition experiments (S. V. A.) indicated that this does not take place. The present investigations also show that the double bond is definitely activated even with two phenyl groups symmetrically located.

EXPERIMENTAL

The reaction velocities were measured by the usual methods as described in Part I, the same accuracy in thermostat control being maintained. Bromine was prepared by the method described by Anantakrishnan and Ingold[2] and its purity tested by the criterion indicated by one of us.[1] Pure Fumaric acid (Kahlbaum's) was repeatedly recrystallised from alcohol to

constant melting point 290° C. in a sealed tube. The substance was stored in a vacuum desiccator till used.

Stilbene was prepared from benzoin by the method of Ballard and Dehn[4] and the pure trans form used in the investigation.

Summary

A study of the reaction between bromine and fumaric acid and bromine and stilbene brought out clearly the validity of the rate equation derived in the previous part. The uncatalysed addition reaction of fumaric acid exhibits the characteristics of a degenerate branching chain.

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KINETICS OF THE OLEFINE-BROMINE REACTION

Part VI. Further Consideration of the Arrhenius Parameters

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It is well known that in the treatment of any kinetic problem the activation energy is a factor of fundamental importance. In any reacting system, the reactants and products represent states of minimum potential energy, while the transition state must be a maximum in between these limits of minima. The reaction involves the breaking of bonds and the formation of new ones and the work done in the process constitutes the activation energy. When the reaction of a series of similar compounds are studied, the principal difference that may be expected is in the activation energy. One cannot, however, consider the variation in the other Arrhenius parameter negligible as has been demonstrated by the work of Hinshelwood and co-workers.[5, 7, 8]

Though the number of compounds investigated in the present series is as yet small, one has still to consider these parameters as the influence of substituent groups on these is of considerable diagnostic value and is of greater significance than any measurement of velocity constants at a single temperature. Since the reaction in question involves the change of a double bond to a single one, rupture of the bond between the atoms of the bromine molecule and the formation of carbon-bromine bonds, one may expect a more or less constant frequency factor† while the activation energy shows systematic variations. The results of evaluating these and the Log k/1/T curve used for the purpose are given below in Table I and Fig. 1.

An examination of both the figure and the table clearly shows that substituents alter both the energy of activation and the frequency factor. The activation energy in its turn can be further analysed into the bond energy

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† The quantity of the Arrhenius equation which is approximately kT/h and hence has the dimensions of frequnecy. This term is preferred to the older 'probability factor'.

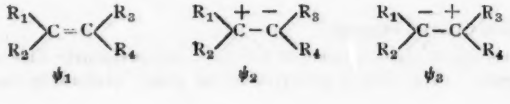
TABLE I

Substance	Concentration in moles/l	Temperature °C.	100 k_2 moles/l min.$^{-1}$	E Calories	PZ $\times 10^{-5}$
Crotonic acid .. (*trans*)	M/15	25·15	4·360	less than 3000	
		35·40	7·169		
		42·50	10·30	10,800	1·952×10 at 35·5° C.
		49·95	15·12		
	M/30	25·15	2·213		
		35·40	3·787		
		42·50	5·860	10,800	19·52 at 35·5° C.
		49·95	8·523		
Tiglic acid ..	M/15	30·20	40·15		
		35·50	49·99		
		42·25	62·09	6·800	0·136 at 35·5° C.
		50·05	78·94		
	M/30	30·10	16·66		
		35·50	19·95		
		42·25	24·35	6·800	0·136 at 35·5° C.
		50·05	31·52		
$\beta\beta$ Dimethyl acrylic acid	M/30	35·5	77·80		
		42·6	91·68	4·500	
		50·3	108·4		
	M/60	35·5	33·94		
		42·6	42·02	7,200	0·443 at 35·5° C.
		50·3	53·57		
Fumaric acid ..	M/30	35·50	0·2097		
		43·30	0·4950	21,270	2·66×10^7 at 35·5° C.
		50·60	1·254		
Stilbene (trans) ..	M/600	35·50	81·5		
		43·30	107·9	7,700	1·995 at 35·5° C.
		50·6	150·8		

Key to numbers: 1. Crotonic acid. 2. Tiglic acid. 3. Dimethyl acrylic acid. 4. Fumaric acid, 5. Stilbene.

and repulsion energy and substituents can alter either or both of these. Hinshelwood, Laidler and Timm[8] from a study of the same reaction in a series of aromatic compounds find that the changes occur only in the bond energy. A difference may, however, arise in the present type of reaction arising primarily from the nature of the olefin.

The ground state of an olefine results from resonance among the structures



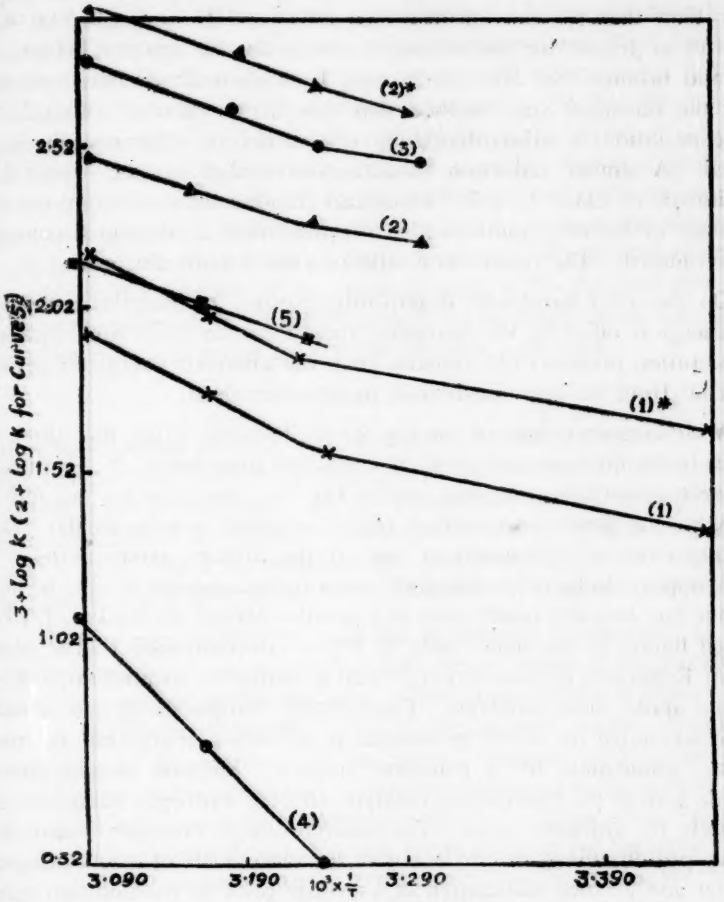


FIG. 1. log k/1/T curve

and forms ψ_2 and ψ_3 will have identical energies only in the case of symmetrically substituted olefines. Additive reactivity depends primarily on the opening up of the double bond and will naturally depend on the relative contribution of the different structures which in its turn determines the bond energy as well as the repulsion energy. With unsymmetrically substituted olefines the contribution by the ionic structures can be quite appreciable and when this is combined with the presence of groups that facilitate reaction with electrophilic reagents on account of their influence on the state of polarisation of the molecule, the activation energy can be substantially

lower than that for the unsubstituted ethylene. No experimental data is available at present for the activation energy, for the reaction between ethylene and bromine but Sherman[13] using Eyring's method[3] has evaluated by using the transition state method that this has a value of about 23 Kcal. The expectation is substantiated by our values for the monobasic acids studied. A similar reduction in activation energy can be expected with substituents of Class 7 ($\pm$ T)[9] which can stabilise the carbonium ion of the first stage of bromine addition even if symmetrical disubstituted compounds are considered. The results with stilbene clearly bears this out.

On the other hand with deactivating groups, an increase in the activation energy is offset by the resonance energy, so that even with symmetrical disubstitution products like fumaric acid, the observed energy of activation is not far from the calculated value for ethylene itself.

A close examination of the log $k - 1/T$ curve of the first three compounds in the table reveals a definite change of slope below 25° C., indicating that the reaction is a composite one.[6] The very low value for the activation energy in the lower temperature region suggests a termolecular reaction changing over to a bimolecular one at the higher temperatures. This feature appears to be independent of concentration changes as may be noticed from the fact that this results only in a parallel shift of the log $k - 1/T$ curve. (Starred figures in the figure refer to higher concentrations.) The observations of Robertson and co-workers[12] with a number of olefines at 25° C. then becomes quite understandable. Considerable variations in rate constants can be accounted for solely by changes in activation energy but our present data are inadequate for a complete analysis. Mention should, however, be made here of the pronounced catalytic effect of hydrogen halides (or more accurately by hydrogen ions). The calculations of Polanyi[1, 11] have shown that the proton affinity of ethylene is of the same order of magnitude as that of water and as such association of a proton prior to the addition reaction can be expected to facilitate the change by providing a seat of attack. A corollary to this one has to expect that attack by nucleophilic bromine will not be facilitated by the same catalyst.

Turning now to the other parameter, namely, the frequency factor, a normal second order reaction requires a value of the order of 10^9 while the values in the table show considerable variations from this. A point of particular interest is the fact that fumaric acid appears to react much faster than it should (a bimolecular reaction with an activation energy of 20 Kcal. should give a rate constant of the order of 10^{-12} with a frequency factor of normal value but observed values are much higher. The remaining four

compounds react with bromine at rates that bring them under the category of "slow" reactions. This is only to be expected when one considers the nature of the reaction. For the reaction to take place, encounters have to be made between molecules possessing the requisite activation energy. Secondly, the initiation of attack is by an electrophilic reagent. Further, the encounter between the reactants must be in the right phase in the region of the double bond. As a first approximation, one can consider that the ratio of the number of effective collisions, z^*, to the total number of collisions calculated in the usual manner, z, will be proportional to the area of the strip cut on the spheroid of the dimensions of the molecule by two parallel planes perpendicular to the direction of the reacting bond, a_s, to the total area of the surface of the spheroid, a. Taking the surfaces as functions of the square of bond distance r_b and major axis of the ellipse r_m, we have

$$z^*/z \simeq (r_b/r_m)^2.$$

Taking into account the fact that the rate determining step in the reaction involves only one of the two doubly bound carbon atoms, this ratio should be halved in the present case. All the compounds studied here have major axes of the order of 6 – 11 Å while the carbon-carbon double bond distance is only 1·33 Å. As a consequence, the frequency factor may be expected to be reduced from 10^9 to about 10^6, a value not far from the ones obtained.†

A further complication that one has to consider in the study of unsaturated compounds of the polysubstituted olefine group is the isomerisation of *trans* compounds to the *cis* form. This complication is absent only in the case of $\beta\beta$-dimethylacrylic acid in the present series. Unpublished observations of the authors indicate that *cis* crotonic acid is less reactive than the *trans* while maleic acid is considerably more reactive than fumaric acid. It is well known that halogens facilitate the interconversion of these stereoisomeric forms[2, 10] and this can easily account for the observed anomalies in the frequency factor. Another contributory cause for reduction in the frequency factor is the composite nature of the reaction.

In a number of reactions, a close correlation is observed between log PZ and $1/E^{\frac{1}{2}}$[5] and a similar relationship may be looked for in the present reaction also. For the sake of comparison the product of these two quantities has been taken for Table II.

† A more rigorous analysis of this and other "slow" reactions will be communicated shortly.

TABLE II

Substance	Log PZ × 1 /E
Crotonic acid ..	0·056
Tiglic acid ..	0·046
Dimethylacrylic acid ..	0·047
Fumaric acid ..	0·011
Stilbene ..	0·050

It will be observed that the product is constant within the limits of experimental error, the exception being provided by fumaric acid. The significance of this can be considered only after a fuller investigation.

SUMMARY

An analysis of the Arrhenius parameters for the addition reaction indicates that the reaction is a composite one and of the "slow" type. The influence of substituents on the energy of activation and on the frequency factor is discussed and the abnormal values of the latter are accounted for. A close correlation is also noticed between the two.

One of the authors (R. V.) thanks the authorities of the Annamalai University for giving the necessary facilities for experimental work.

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CHEMICAL EXAMINATION OF THE BARK OF *ALANGIUM LAMARKII* THWAITES. ISOLATION OF THE ALKALOID ALANGINE

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Alangium Lamarkii or Ankula as it is known in Bengali and Sanskrit, and Akola in Hindi, is a small handsome evergreen tree belonging to the Natural Order of Alangiaceæ. It is met with throughout India, often growing wild, but sometimes cultivated as an ornamental garden plant for the beautiful, narrow, oblong and prominently reticulated leaves and white wax-like glossy flowers. It is particularly abundant in Chota Nagpur, Orissa, Andhra districts, Central Provinces, United Provinces and South-Eastern Punjab.

The plant is highly medicinal. According to Kirtikar and Basu,[1] the root is acrid, bitter, slightly pungent, heating, anthelmintic, alterative. It cures erysipelas, biliousness, inflammations and snake bites and acts like a fish poison. The bark is emetic, alexipharmic and cures cough, rheumatism, pain, inflammations, biliousness, diseases of the blood, hydrophobia, rat-bite, lumbago, dysentery, diarrhœa and worms. The seeds are cooling, aphrodisiac, indigestible, tonic, nutritive and laxative. They cure burning sensations, consumption, hæmorrhage, biliousness, erysipelas, cough and loss of appetite. They have also a reputation in the cure of leprosy.

The seeds of the plant have already been worked out by Bhargava and Dutt,[2] who isolated from them an interesting sterol having a molecular formula $C_{42}H_{84}O_7$, which they named 'alangol'. Very little fixed oil was found in the seed and no other constituent could be detected.

The bark of the plant has not yet been properly worked by anyone. Dymock[3] has reported the presence of an uncrystallisable alkaloid which could not be obtained in a pure form. According to him all the salts of the base are uncrystallisable. On ignition, the platinum salt gave 20·70% of platinum from which the molecular weight of the base was found to be 265·9. No further work has been done by any one on this subject.

The present authors working on the bark of the plant have been able to isolate an alkaloid crystallising in glistening, yellow prisms and melting at

205–08° C. The molecular formula of the substance which has been named 'alangine' was found to be $C_{19}H_{25}O_2N$, and it behaved like a mono-acid base with one methoxy group. There was an indication of an alcoholic hydroxy group due to the formation of acetyl and benzoyl derivatives, but they did not give good analytical results.

Alangine is strongly basic in nature and forms well-defined and crystalline hydrochloride, iodide, oxalate, tartrate, nitrosate and iodomethylate. It is a tertiary base but does not contain any $>N-CH_3$ group as by Herzig and Meyer's method no indication of such a group in the molecule was obtained.

Alangine is present in the bark of *Alangium Lamarkii* to the extent of 0·1%. The bark besides containing alangine also contains a fair proportion of colouring matters, potassium nitrate, gum, etc. Fresh bark has been found to contain a greater proportion of alangine than the bark which has been stored for some time. The chemical properties and reactions of alangine correspond to no known alkaloid. So it must be a new compound.

Experimental

Extraction of the bark with different solvents

20 gm. of the finely powdered bark were extracted with different solvents in a Soxhlet's apparatus, the solvent evaporated and the residue dried to a constant weight. The percentage of the extract by each solvent is given below:—

Water	15·05
Alcohol	13·98
Acetone	8·22
Chloroform	2·96
Ethyl acetate	3·01
Benzene	1·15

In each of the above extracts the reactions of an alkaloid was given by all the alkaloid reagents. The extracts were also extremely bitter in taste.

Isolation of the alkaloid

200 gm. of the air-dried powdered bark were repeatedly percolated with acidulated water (0·5% HCl) at the ordinary temperature until the last extract obtained did not give any appreciable precipitate with Dragendorff's reagent. The extract gave the following reactions with various alkaloid reagents:—

(1) Dragendorff's reagent	..	Thick orange precipitate.
(2) Wagner's reagent	..	Thick brown precipitate.
(3) Meyer's reagent	..	Deep yellow precipitate.
(4) Phosphotungstic acid	..	Bright yellow precipitate.
(5) Phosphomolybdic acid	..	Thick yellow precipitate.
(6) Platinic chloride	..	Yellow precipitate.
(7) Auric chloride ..	..	Yellow precipitate.
(8) Tannic acid ..	..	Buff coloured precipitate.
(9) Picric acid ..	..	Yellow crystalline precipitate.
(10) Chromic acid ..	..	Yellow-brown precipitate.
(11) Sodium carbonate	..	Yellow precipitate (Free alkaloid).
(12) Conc. Sulphuric acid	..	Light brown colouration.
(13) Luchini's reagent	..	Yellow-brown-violet-green.
(14) Erdmann's reagent	..	Violet-orange.
(15) Conc. Nitric acid	..	Light violet.
(16) Frode's reagent ..	..	Violet, changing to yellow.

The total extract was neutralised with dilute sodium carbonate and the resultant thick yellow precipitate filtered off, washed with water and dried in the air. It was then extracted with hot ammoniated alcohol (0·5%) and the extract after neutralisation with acetic acid, evaporated to a syrup under reduced pressure. The syrupy material was then extracted with ethyl acetate, and the ethyl acetate extract after concentration, precipitated with a mixture of ether and petroleum ether (2 : 1). The resulting granular yellow precipitate was filtered off, washed with petroleum ether and then further purified by repeatedly dissolving it in chloroform and reprecipitating with ether. The purified alkaloid which was thus obtained as a bright yellow powder was finally crystallised from a mixture of chloroform and ether and the process repeated a number of times until no further rise in the melting point was noticed. The base was thus obtained in the form of glistening yellow elongated prisms melting at 205–08° C. with decomposition.

It is sparingly soluble in cold water but more so in the hot. It is easily soluble in alcohol, ethylacetate, acetone, chloroform, carbon disulphide and pyridine but is quite insoluble in benzene, ether and petroleum ether. An aqueous solution of the alkaloid is extremely bitter to taste and is faintly basic towards litmus, phenolphthalein and methyl-orange. The substance is optically active, showing $[\alpha]_D^{22°} = +9°$ in alcohol. A microphotograph of the alkaloid is given showing its finely crystalline form. Found: C =

75·92, 76·02%; H = 8·54, 8·48%; N = 4·75, 4·82% (Duma's); 4·47, 5·04% (Kjeldahl); M.W. = 296,304,297 (Rast's Camphor method); 307,297 (Ebullioscopic in Chloroform); 297·6, 292·3 (ignition of the chloroplatinate); 290·6, 304·0 (ignition of the Chloroauriate); $C_{19}H_{25}O_2N$ requires C = 76·25%, H = 8·36%, N = 4·68%; M.W. = 299.

The alkaloid contains one methoxyl group in the molecule. (Found: OCH_3 = 10·45, 10·25, 10·42 by Zeissel's method. $C_{18}H_{22}ON\ OCH_3$ requires OCH_3 = 10·36%.) The absence of N-methyl was confirmed.

Preparation of the salts of the alkaloid

Alangine hydrochloride.—The hydrochloride of the base was prepared by dissolving it in alcohol and treating with a slight excess of warm alcoholic hydrogen chloride. On cooling and adding a little ether to the solution, the hydrochloride was obtained as yellow crystalline prisms, melting at 264° C. It is easily soluble in water and ordinary organic solvents except benzene, ether and petroleum ether. (Found: Cl = 9·94; $C_{19}H_{25}O_2N.HCl$ requires Cl = 10·58 per cent.)

Alangine sulphate.—This was obtained by adding alcoholic sulphuric acid to an alcoholic solution of the base, and diluting the mother-liquor slightly with ether. The sulphate came down as a light yellow powder melting at 118° C. The salt is sparingly soluble in cold water but is readily soluble in alcohol, chloroform and acetone. It is insoluble in ether, benzene and petroleum ether. (Found: S = 4·59, 4·71; $(C_{19}H_{25}O_2N)_2.H_2SO_4$ requires S = 4·60%.)

Alongine nitrate.—This was obtained in a similar way as the hydrochloride and the sulphate, from alangine and alcoholic nitric acid. It is a yellow crystalline powder melting at 176° C. The properties of this substance are similar to those of the other inorganic salts.

Alangine iodide.—To a hot aqueous solution of the chloride was added a concentrated solution of potassium iodide. The iodide separated as a deep yellow crystalline precipitate. It was recrystallised from ether-alcohol mixture in the form of yellow prisms melting at 178° C. with decomposition. The substance is sparingly soluble in water but readily in alcohol. It is insoluble in ether and petrol ether. (Found: I = 29·38; $C_{19}H_{25}O_2N.HI$ requires I = 29·74%.)

Alangine acetate, tartrate and oxalate.—These were prepared by the action of alcoholic acetic, tartaric and oxalic acids on alcoholic solutions of alangine. They are all yellow, crystalline substances with properties

similar to those of the chloride. Alangine acetate melts at 202° C., tartrate at 220° C. and oxalate at 89° C.

Alangine picrate.—To a solution of the base in dilute hydrochloric acid was added a saturated aqueous solution of picric acid when a light-yellow, crystalline powder came down. This was recrystallised from ether-alcohol mixture in glistening flakes, melting at 84° C. It is soluble in alcohol, chloroform, ethyl acetate and acetone and sparingly in benzene. It is insoluble in ether and petrol ether. (Found: N = 10·34; $C_{25}H_{28}O_9N_4$ requires N = 10·60%.)

Alangine-iodomethylate.— To a solution of the base (1 gm.) in chloroform (3 c.c.), methyl iodide (1 c.c.) was added and the mixture strongly cooled. On allowing to stand for about two hours, a deep yellow crystalline substance separated out. This was filtered, washed with chloroform and dried under vacuum at room temperature (21° C.). It melts at 201° C. with decomposition. (Found: I = 28·53; $C_{20}H_{28}O_2NI$ requires I = 28·79%.)

The quaternary salt is very soluble in water and alcohol, but the solubility decreased in the order—ethyl acetate, chloroform, acetone and benzene. It is completely insoluble in ether and petrol ether.

Summary and Conclusion

1. From the bark of *Alangium Lamarkii* Thwaites, a new alkaloid has been obtained crystallising in long yellow glistening prisms, m.p. 205—08° C. The molecular formula of the alkaloid has been found to be $C_{19}H_{25}O_2N$. This has been named "Alangine".

2. The alkaloid has been found to be a monoacid base containing one methoxy group but no $>N-CH_3$ group.

3. The alkaloid which is dextrorotatory easily gives crystalline salts with organic and inorganic acids and the hydrochloride, sulphate, nitrate, iodide, acetate, tartrate, oxalate, picrate and iodomethylate have been prepared and described.

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COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE METALLIC DERIVATIVES OF ISONITROSODIPHENYL-THIOBARBITURIC ACID

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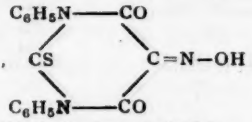
Violuric acid and its highly coloured organic and inorganic salts have been investigated from the point of view of colour in relation to chemical constitution by a large number of workers. Hartley,[1] Hantzsch,[2] Meek and Watson[3] have shown that the greater the basic character of the base, the greater is the intensity of the colour of the salt formed.

The next interesting work in this connection was done by Lal and Dutt[4] who took up the study of isonitrosothiobarbituric acid or thiovioluric acid which was prepared by them for the first time by the action of nitrous acid on thiobarbituric acid. The alkali and organic salts of this compound were found to be highly coloured substances, far more so than the corresponding salts of violuric acid, which was due to the introduction of a sulphur atom in place of an oxygen atom. The effect of sulphur on the colour of the organic compounds and dyestuffs was previously noticed by Purvis, Jones and Tasker,[5] who noticed that the thio-oxalates of alkalies are yellow in colour whereas the corresponding oxalates are colourless. Further Lal and Dutt examined the absorption spectra of thioviolurates and also the dissociation constants of a number of them which were soluble in water, but on comparing the results thus obtained, they came to the conclusion that the colour of thioviolurates is not intimately connected with electrolytic dissociation and in fact, intense colours were possessed by compounds which were altogether insoluble in water or hydroxylic solvents and whose absorption spectra had to be determined in acetone or chloroform solutions.

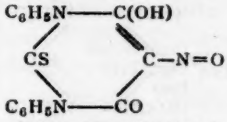
As a result of the work of Lal and Dutt on thiovioluric acid, Prakash and Dutt[6] thought that any further loading of the molecule of violuric acid by heavy substituents might lead to further accentuation of colour. They prepared sym-diphenyl-violuric acid and showed that the organic salts derived from weak bases like pyridine and aniline have colours no less intense than the alkali salts. The possibility of molecular ionisation having

been ruled out, the most reasonable explanation of the origin of colour in these compounds was thought to lie in a fundamental change in the constitution of the molecule on salt formation in accordance with the theory of colour on the basis of molecular strain advanced by Dutt.[7, 8]

The present authors prepared the inorganic salts of diphenyl-thio-violuric acid and found accentuation of colour in accordance with the above theory. The deepening of colour during salt formation lies in a change in the structure of the molecular from the oximino-ketonic to the nitroso-enolic form which is more strained according to the theory of colour on the basis of molecular strain, advanced by Dutt. The organic salts of diphenyl-thiovioluric acid have already been worked by Dass and Dutt.[9]



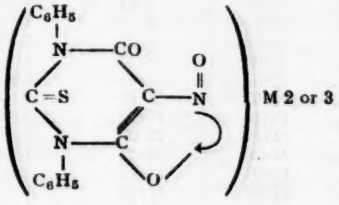
"Oximino-ketonic form"



"Nitroso-enolic form"

Theoretical considerations show that the metallic salts of diphenyl-thiovioluric acid are probably of the nature of internally complex compounds. The acid molecule in its nitrosoenolic form contains one replaceable hydrogen which is replaced by the metal atom during salt formation.

The possibility of inner complex salt formation arises wherever acidic and donor functions (such as amino, carbonyl, etc., groups) are suitably placed in the same molecule, *i.e.*, in 1 : 4 or 1 : 5 position to one another. This is the case with diphenyl-thio-violuric acid where nitrogen atom of the nitroso group can act as a donor and bring about ring-formation. Their stability, low melting points, solubility in organic solvents also support the view that they are inner complex salts. The salts of bi and trivalent metals may be given the following general formulæ where M is the metal atom:—



EXPERIMENTAL

Preparation of diphenylthiovioluric acid.—A mixture of thiocarbanilide (10 gm.), malonic acid (6 gm.) and acetyl chloride (9 c.c.) was heated on a

TABLE I. *Properties of Salts*

	Name of the metal	Colour in solid state	Colour in acetone	M.P. °C	Absorption maxima A°
1	Silver ..	Light Green	Green	216	..
2	Lead ..	Light Brown	Brown	200	5050
3	Mercuric ..	Green	Greenish Yellow	225	7200
4	Bismuth	Orange Brown	..	201	4850
5	Copper ..	Brown	Light Brown	224	5250
6	Cadmium ..	Brown	Reddish Brown	256	..
7	Antimony ..	Orange	Yellowish Orange	218	5200
8	Tin ..	Brick Red	Light Red	..	..
9	Ferrous ..	Deep Blue	Deep Blue	220	6650
10	Ferric ..	Dark Green	Green	210	6520
11	Aluminium ..	Buff Coloured	Buff	212	4680
12	Chromium ..	Green	Green	211	5320
13	Cobalt ..	Dark Brown	Dark Brown	255	5720
14	Nickel ..	Yellowish Brown	Yellowish Brown	315	5600
15	Manganese ..	Slate Coloured	Blue (Light)	295	4980
16	Zinc ..	Light Brown	Brown	264	4850
17	Calcium ..	Light Pink	Almost Insoluble	above	5080
18	Strontium ..	Pink	Pink with Blue tinge	350°	5120
19	Barium ..	Dark Pink	..	..	5150
20	Magnesium	Light Brown	Light Brown	..	4820
21	Cerium ..	Pale Yellow	Pale Yellow	230	4870
22	Gold ..	Dark Brown	Brown	200	5150
23	Platinum ..	Buff Coloured	Light Brown	204	4750
24	Uranium ..	Reddish Brown	Reddish Brown	219	..
25	Ammonium ..	Bluish Grey	Greenish Blue	213	6060
26	Potassium ..	Deep Emerald Green	Brilliant Green	219	6560
27	Sodium ..	Greenish Black	Intense Emerald Green	128	6610

Estimation of Metal and Sulphur

	Metallic salt	% of metal observed	Theoretical % of Metal	Ratio of Metal to Acid	% of Sulphur observed	Theoretical
1	Sodium ..	..	..	..	9·39	9·22
2	Potassium ..	..	..	..	8·84	8·81
3.	Ammonium ..	..	..	..	9·86	9·35
4	Silver ..	24·93	24·97	1 : 1	7·28	7·42
5	Ferrous ..	7·87	7·93	1 : 2	9·04	9·11
6	Ferric ..	5·46	5·43	1 : 3	9·28	9·36
7	Aluminium ..	2·68	2·70	1 : 3	9·75	9·63
8	Chromium ..	5·10	5·01	1 : 3	9·37	9·40
9	Nickel ..	8·27	8·30	1 : 2	9·00	9·07
10	Copper ..	8·89	8·93	1 : 2	9·11	9·01
11	Cobalt ..	8·30	8·34	1 : 2	9·16	9·07
12	Magnesium ..	3·55	3·62	1 : 2	9·42	9·53
13	Calcium ..	7·54	7·61	2 : 3	6·01	9·14
14	Strontium ..	15·16	15·28	2 : 3	8·30	8·38
15	Barium ..	22·17	22·03	2 : 3	7·81	7·71
16	Lead ..	24·20	24·23	1 : 2	7·45	7·50
17	Antimony ..	10·97	11·13	1 : 3	8·70	8·80
18	Bismuth ..	17·62	17·70	1 : 3	8·09	8·14
19	Zinc ..	9·10	9·16	1 : 2	9·00	8·98
20	Cadmium ..	14·67	14·78	1 : 2	8·49	8·43
21	Mercuric ..	23·10	23·64	1 : 2	7·46	7·55
22	Manganese ..	7·80	7·81	1 : 2	9·13	9·12
23	Gold ..	16·24	16·86	1 : 3	8·25	8·22
24	Cerium ..	9·62	9·77	1 : 4	6·74	6·69
25	Platinum ..	22·90	23·15	1 : 2	7·39	7·60
26	Uranium ..	26·01	26·77	1 : 2	6·98	7·23

water-bath under reflux for about half an hour. The solid yellow mass was broken up, ground with water in a mortar, filtered, washed, dried and crystallised from glacial acetic acid when yellow needles of m.p. 245° C. were obtained.

Diphenyl-thiobarbituric acid as obtained above (20 gm.) was dissolved in KOH solution (5%) and a solution of sodium nitrite (20 gm.) in minimum quantity of water was added. The mixture was filtered, cooled in ice and gradually acidified with ice-cold dilute sulphuric acid. The light buff-coloured precipitate was allowed to stand overnight, filtered, washed with water and dried and crystallised from boiling glacial acetic acid when it was obtained in glistening prisms melting at 227° C.

Preparation of the metallic salts.—The ammonium salt was prepared by adding concentrated ammonia to a saturated solution of the acid in acetone till slightly alkaline, when the ammonium salt was obtained as a bluish-grey glistening crystalline precipitate which after drying was recrystallised from water.

Other salts were prepared by adding a solution of a salt of the metal whose salt was to be prepared to a solution of the ammonium salt in water when the metallic derivative was thrown down as a precipitate. This was washed with hot water, crystallised from acetone and the percentages of metal and sulphur were estimated by the usual methods.

The silver salt is photo-sensitive and decomposed very slowly on keeping. Other salts are quite stable and melt above 200° C. with decomposition. All the salts of diphenyl-thiovioluric acid possess beautiful crystalline structure and are highly soluble in acetone and less so in alcohol or ether. The absorption maxima of a number of them were also found out.

Summary and Conclusions

1. The metallic salts of *iso*-nitroso-diphenyl-thiobarbituric acid have been prepared for the first time with a view to study their colour in relation to chemical constituents.

2. The change of colour from yellow to blue or green has been shown from theoretical considerations to be due to a fundamental change in the constitution of the molecule from an oximino-ketonic to a nitroso-enolic structure.

3. The change in structure produces a true nitroso group which from the point of view of the theory of colour on the basis of molecular strain,

has been shown to be a highly strained group which thus gives intense colour to the salts.

4. From theoretical considerations, the salts appear to be internally complex compounds and structural formulæ have been given on this basis.

The authors wish to express their indebtedness and sincere thanks to Prof. S. Dutt for his kind interest in the work.

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1-NITRO-2-HYDROXY-3-NAPHTHOIC ACID AND ITS DERIVATIVES

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6-Nitro-2-hydroxy-3-naphthoic acid is obtained by the nitration of 1-amino-2-hydroxy-3-naphthoic acid or its diazo-oxide and subsequent elimination of the amino or diazo group (*I. G. Farbenind.* A. G., Ger. 623496; General Aniline Works, U.S. 2040587; *I. G. Farbenind.* A. G., Brit. 445278). This 1-amino-2-hydroxy-3-naphthoic acid has been prepared by various indirect methods (Mohlau, *Ber.*, 1893, **26**, 3066; Mohlau and Kriebel, *Ber.*, 1895, **28**, 3091; Weil and Heerdt, *Ber.*, 1922, **55**, 226). Robertson (*J. pr. ch.*, 1893, (2), **48**, 534), however, claims to have obtained it by the reduction of 1-nitro-2-hydroxy-3-naphthoic acid which in its turn is obtained by the nitration of 2-hydroxy-3-naphthoic acid, but no experimental details are available and the melting point of the nitro acid given by this author is 233–38° which is quite different from the one described here (246–48°) and therefore his nitro acid may not be pure.

Later Gradenwitz (*Ber.*, 1894, **27**, 2623) nitrated methyl 2-hydroxy-3-naphthoic acid and got simple phthalic acid by the oxidation of the nitro derivative obtained. He thus proved isonuclear positions of –OH, –COOH and $-NO_2$ groups, but he did not definitely name the susbtance. But the only possible position taken up by the nitro group, according to the directing influences of –OH and –COOH groups, is 1 only. His nitro derivative must, therefore, be methyl 1-nitro-2-hydroxy-3-naphthoate.

In the present work the methyl and ethyl esters of 2-hydroxy-3-naphthoic acid are nitrated according to Gradenwitz (*loc. cit.*) and free acid is obtained by hydrolysis with alcoholic potassium hydroxide. 1-Nitro-2-hydroxy-3-naphthoic acid melts at 246–48°.

The ethyl ester of the nitro acid has the melting point 155–56°, identical with that described by Meisenheimer, Theilcker and Beißwenger (*Ann.*, 1932, **495**, 275) who have not given experimental details.

The acid chloride of 1-nitro-2-hydroxy-3-naphthoic acid is easily obtained. From this acid chloride, some derivatives like ethyl esters and arylamides are prepared from aniline, *o*-, *m*-, and *p*-toluidines and *o*-, *p*-, anisidines.

Experimental

1-Nitro-2-hydroxy-3-naphthoic acid.—A mixture of methyl 1-nitro-2-hydroxy-3-naphthoate (or the ethyl ester) (10 g.), rectified spirit (50 c.c.) and potassium hydroxide (100 c.c. of 2 N) was refluxed on boiling water-bath for about two hours. The acid, that separated on acidification, was crystallised from dilute alcohol in shining yellow needles, m.p. 246–48°. (Found: N, 6·0%; $C_{11}H_7O_5N$ requires N, 6·0%.)

1-Nitro-2-hydroxy-3-naphthoyl chloride.—A mixture of 1-nitro-2-hydroxy-3-naphthoic acid (1 g.), phosphorous pentachloride (2 g.) and dry chloroform (25 c.c.) was refluxed on boiling water-bath until a clear solution was obtained. On cooling the reaction mixture, the acid chloride separated in brownish yellow needles, which were filtered and washed with dry petroleum ether and dried under vacuum over phosphorous pentoxide, m.p. 168–70°. (Found: Cl, 14·2%. $C_{11}H_6O_4NCl$ requires Cl, 14·1%.)

Phenyl-1-nitro-2-hydroxy-3-naphthoate.—It is prepared by heating together a mixture of acid (2 g.), phosphorous oxychloride (1 c.c.) and phenol (2 g.) at 140-50° until effervescence ceases. The mixture is cooled, diluted with water and washed.

Table I

Derivatives of 1-nitro-2-hydroxy-3-naphthoic acid

	Name	Formula	Appearance	Melting point	Nitrogen	
					Found	Required
1	Phenyl-1-nitro-2-hydroxy-3-naphthoate	$C_{17}H_{11}O_5N$	Thick flat needles	170–71°	4·7%	4·5%
2	Ethyl-1-nitro-2-hydroxy-3-naphthoate	$C_{13}H_{11}O_5N$	Yellow needles	155–56°	5·1%	5·4%
3	1-Nitro-2-hydroxy-3-naphthanilide	$C_{17}H_{12}O_4N_2$	Small yellow needles	188–89°	9·5%	9·1%
4	1-Nitro-2-hydroxy-3-naphtho-toulidide	$C_{18}H_{14}O_4N_2$	Orange needles	190–91°	9·2%	8·7%
5	1-Nitro-2-hydroxy-3-naphth *m*-toulidide	$C_{18}H_{14}O_4N_2$	Pale yellow needles	196–97°	9·0%	8·7%
6	1-Nitro-2-hydroxy-3-naphtho-toulidide	$C_{18}H_{14}O_4N_2$	Long pale yellow needles	199–200°	9·3%	8·7%
7	1-Nitro-2-hydroxy-3-naphtho-anisidide	$C_{18}H_{14}O_5N_2$	Yellow flat needles	224–25°	8·4%	8·3%
8	1-Nitro-2-hydroxy-3-naphtho-anisidide	$C_{18}H_{14}O_5N_2$	Yellow needles	210–11°	8·9%	8·3%

The arylamides are prepared by leaving the mixture of the amine and acid chloride in presence of dry benzene for an hour and washing the solid obtained with dilute hydrochloric acid after the removal of the solvent. They are crystallised from glacial acetic acid. They are described in Table I.

SUMMARY

Free 1-nitro-2-hydroxy-3-naphthoic acid is isolated, its acid chloride, phenyl ester and anilide, *o*-, *m*-, *p*-toulidides and *o*- and *p*-anisidides are prepared.

THE ACTION OF HEXAMETHYLENETETRAMINE ON THE METHYL ESTERS OF PHENOL-CARBOXYLIC ACIDS

Part V. The Derivatives of 2: 4-Dihydroxy-5-Formylbenzoic Acid

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The preparation as well as the characterisation of 2: 4-dihydroxy-5-formylbenzoic acid has already been described by Desai and Radha.[1] Some of its important and interesting derivatives are being described in this communication. Attempts to esterify the carboxyl group by Fischer-Speier method resulted in the formation of some colouring matter. The action of either diazomethane, or dimethylsulphate in an alkaline medium or the action of methyl iodide on the silver salt of the acid resulted in the methylation of only one of the hydroxyl groups, and various other methods of methylation failed to give the dimothoxy derivative. The monomethoxy derivative may be either 2-methoxy-4-hydroxy-5-formylbenzoic or 2-hydroxy-4-methoxy-5-formylbenzoic acid.

Nitration of 2: 4-dihydroxy-5-formylbenzoic acid gave a mixture of 2: 4-dihydroxy-5-nitrobenzaldehyde and 2: 4-dihydroxy-3 : 5-dinitrobenzoic acid, and it was not possible to isolate the nitro-derivative containing both the formyl and carboxyl groups in tact.

Clemmenson reduction gave readily 2: 4-dihydroxy-5-methyl-benzoic acid, while bromination of the aldehyde acid under various conditions gave a bromo-derivative which gave too low values for the halogen. Acetylation of the aldehydo acid with acetic anhydride in presence of either pyridine or anhydrous sodium acetate gave only the di-acetoxy derivative, not a trace of the coumarin which was expected in the latter method being formed.

Condensation of the aldehydo acid with ethyl malonate and ethyl acetoacetate by Knoevenagel's method gave respectively 3-carbethoxy-6-carboxy-7-hydroxy coumarin and 3-acetyl-6-carboxy-7-hydroxy coumarin, the alkaline solutions of which gave blue fluorescence. The formation of these two coumarin derivatives furnish the additional proof to establish the 5-position of the formyl group.

Experimental

Methylation of 2:4-*dihydroxy*-5-*formylbenzoic acid and formation of* 2 *or* 4-*methoxy*-4 *or* 2-*hydroxy*-5-*formylbenzoic acid.*—To the aldehydo-acid (1 gm.) dissolved in potassium hydroxide (100 c.c. of 20%), dimethylsulphate (20 c.c.) was gradually added with shaking and warmed on the water-bath for one hour. The yellow, flocculent precipitate obtained on the acidification with hydrochloric acid crystallised from methyl alcohol in small yellowish needles, m.p. 246–47. It gave an intense red coloration with alcoholic ferric chloride. (Found: C, 54·8; H, 3·9; $C_9H_8H_5$ requires C, 55·1; H, 4·0 per cent.)

Nitration of 2:4-*dihydroxy*-5-*formylbenzoic acid and formation of* 2:4-*dihydroxy*-5-*nitrobenzaldehyde and* 2:4-*dihydroxy*-3:5-*dinitro-benzoic acid.*—Concentrated nitric acid (15 c.c.) was gradually added with constant stirring to the solution of the aldehydoacid (2 g.) dissolved in concentrated sulphuric acid (10 c.c.), and left in a frigidaire overnight. The solid that separated out was filtered, washed and crystallised from dilute alcohol in long, lustrous, golden-yellow needles, m.p. 146–47°. It did not dissolve in sodium bicarbonate solution, but readily reacted with 2:4-dinitrophenylhydrazine and identified as 2:4-dihydroxy-5-nitrobenzaldehyde of Gattermann.[3] (Found: N, 7·4; $C_7H_5O_5N$ requires N, 7·7 per cent.)

The 2:4-*dinitrophenylhydrazone* prepared in the usual manner crystallised from glacial acetic acid in small, orange needles, m.p. 258° (dec.). (Found: N, 19·5; $C_{13}H_9O_8N_5$ requires N, 19·3 per cent.)

The filtrate from which the nitro-aldehyde was removed was diluted with water, salted, and extracted with ether. On the removal of the solvent small yellow crystals of a solid, m.p. 195–96°, were obtained. It dissolved in sodium bicarbonate solution with effervescence, but did not react with 2:4-dinitrophenylhydrazone, and was identified as 2:4-dihydroxy-3:5-dinitrobenzoic acid by comparison with an authentic specimen prepared by Hemmel Meyer's[3] method. (Found: N, 11·2; $C_7H_4O_8N_2$ requires N, 11·5 per cent.)

2:4-*Dihydroxy*-5-*methylbenzoic acid* was prepared by adding the alcoholic solution of the aldehydo acid (2 g.) to amalgamated zinc (40 g.) and dilute hydrochloric acid (50 c.c.) and warming the mixture on the water-bath for 2 hours. The hot liquid deposited small needles, m.p. 163–64° C. (Found: C, 58·2; H, 4·5; $C_8H_8O_4$ requires C, 58·3; H. 4·8 per cent.)

2:4-*Diacetoxy*-5-*formylbenzoic acid* was obtained by heating the mixture of the formyl acid (1 g.), acetic anhydride (10 c.c.) and pyridine (3 drops)

125-126° C. (depressed to 90-91° by β-naphthol). Its alcoholic solution did not give any colouration with ferric chloride. It was insoluble in dilute caustic soda solution, but soluble in most of the organic solvents (yield = 30 p.c.) (Found: C, 81·7; H, 10·1; $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·2 per cent.)

The p-*nitrophenylhydrazone* was prepared by heating the ketone (0·5 g.) and 4-nitrophenylhydrazine (0·5 gm.) in alcohol (20 c.c.) under reflux for six hours. The hydrazone crystallised in reddish lustrous plates m.p. 260–61° C. (Found: N, 7·5; $C_{34}H_{47}N_3O_3$ requires N, 7·7 per cent.)

1-*Stearyl*-2-*methoxy-naphthalene.*—A mixture of 1-stearyl-2-naphthol (1 g.) anhydrous potassium carbonate (2 g.) dimethyl sulphate (5 c.c.) and dry acetone (20 c.c.) was refluxed on water-bath for 6 hours. The solution was filtered and after the removal of acetone the methylated product crystallised from petroleum ether in white, lustrous needles, m.p. 72·73° C. (Found: C, 82·2; H, 10·2; $C_{29}H_{44}O_2$ requires C, 82·1; H, 10·4 per cent.)

Clemmenson reduction of 1-*stearyl*-2-*naphthol-preparation of* 1-*Octadecyl* 2-*naphthol.*—A mixture of dilute hydrochloric acid (1 : 1; 35 c.c.), amalgamated zinc (5 g.), and 1-stearyl-2-naphthol (1 g.) dissolved in alcohol (20 c.c.), was heated on sand-bath under reflux for 6 hours. The cold mixture was diluted with water and extracted with ether. The ethereal layer was extracted with alkali, and the alkaline solution when acidified gave a white product which crystallised from alcohol in white plates, m.p. 75–76° C. (Found: C, 84·5; H, 11·3; $C_{28}H_{44}O$ requires C, 84·4; H, 11·1 per cent.)

Kostanecki reaction with 1-*stearyl*-2-*naphthol and formation of* 2-*methyl*-3-*hexodecyl*-1 : 4-β-*naphthapyrone.*—A mixture of 1-stearyl-2-naphthol (1 g.), powdered anhydrous sodiumacetate (1 g.) and acetic anhydride (10 c.c.) was heated in an oil-bath at 175–180° C. for 14 hours and then poured in water. The white product which separated out was crystallised from alcohol in white, lustrous, small needle, m.p. 79–80° C. It was soluble in usual organic solvents and dissolved in concentrated sulphuric acid giving a reddish brown colour. (Found: C, 82·8; H, 9·6; $C_{30}H_{42}O_2$ requires C, 82·9; H, 9·7 per cent.)

Hydrolysis of the pyrone to stearyl-2-*naphthol.*—The pyrone was boiled with 10 per cent. alkali under reflex for three hours. On acidifying the alkaline solution, a white product was obtained, which crystallised from alcohol in white needles, m.p. 125–126° C. and was identified as stearyl-2-naphthol by mixed m.p.

Condensation of 1-*stearyl*-2-*naphthol with ethyl bromacetate and the preparation of ethyl*-1-*stearyl*-p-*naphthoxyacetate.* A mixture of 1-stearyl-2-naphthol (4 g.), potassium carbonate (1 g.), ethyl bromacetate (4 c.c.) and dry acetone (35 c.c.) was heated on water-bath under reflux for five hours. On removing acetone, a yellowish brown liquid was obtained which was washed with water, extracted with ether, dried and recovered. It was a pale-yellow, oily liquid b.p. 279° C. (Found: C, 77·4; H, 9·8; $C_{32}H_{48}O_4$ requires C, 77·3; H, 9·7 per cent.)

Hydrolysis of ethyl-1-*stearyl*-β-*naphthoxy acetic acid and the preparation of* 1-*stearyl*-β-*naphthoxy acetic acid.*—The above ester (1 g.) was boiled with 10% alcoholic alkali (20 c.c.) under reflux for three hours. On removing alcohol and acidifying the alkali solution, a white product was obtained which was crystallised from alcohol in white flakes, m.p. 66–67° C. (Found: C, 76·8; H, 9·6; $C_{30}H_{44}O_4$ requires C, 76·9; H, 9·5 per cent.)

The p-*nitrophenyl-hydrazone* of the acid prepared by the usual manner crystallised from alcohol in deep-red shining plates m.p. 220–221° C. (Found: N, 6·9; $C_{38}H_{49}O_5N_3$ requires N, 7·0 per cent.)

Action of sodium ethoxide on ethyl-1-*stearyl*-β-*naphthoxy acetate and the preparation of* 2-*carbethoxy*-3-*heptadecyl*-β-*naptha coumarone.*—The β-naphthoxy acetate (5 c.c.) was mixed with sodium ethoxide in absolute alcohol (Na = 2 gm.; alcohol = 40 c.c.) and the solution was heated on water-bath under reflux for three hours. On evaporating the alcohol, a colourless liquid was obtained B.P. 265° C. (Found: C, 80·5; H, 9·8; $C_{32}H_{46}O_3$ requires C, 80·3; H, 9·7 per cent.)

Hydrolysis of the above naphthacoumarone to 2-*carboxy*-3-*heptadecyl*-β-*naphtha coumarone.*—The above ester (3 g.) was boiled with 10 per cent. alcoholic alkali (30 c.c.) for three hours. The solid obtained on the removal of alcohol and acidification from hexane in white, flat needles m.p. 60–61° C. (Found: C, 79·8; H, 9·5; $C_{30}H_{42}O_3$ requires C, 79·9; H, 9·3 per cent.)

Decarboxylation of 2-*carboxyl*-3-*heptadecyl*-β-*naphtha coumarone to* 3-*heptadecyl*-β-*naphtha coumarone.*—The above acid was introduced in a flask and heated at 80° C. for four hours. The brown product obtained after washing the residue with dilute alkali crystallised from hexane in white, small needles, m.p. 49–50° C. (Found: C, 85·5; H, 10·5; $C_{29}H_{42}O$ requires C, 85·7; H, 10·4 per cent.)

1-*Palmityl*-2-*naphthol* prepared from β-naphthol (7 g.), palmitic acid (16 g.) and zinc chloride (7 g.) crystallised from alcohol in white, small plates, m.p. 115–16° C. (depressed to 85–86° C. by β-naphthol). Its

alcoholic solution gave no colouration with ferric chloride (yield 28 per cent.). (Found: C, 81·8; H, 9·7; $C_{25}H_{38}O_2$ requires C, 81·7; H, 9·9 per cent.)

The p-*nitrophenylhydrazone* of the ketone was crystallised from alcohol in red flakes, m.p. 195–96° C. (Found: N, 8·1; $C_{32}H_{43}O_3N_3$ requires N, 8·1 per cent.)

1-*Palmityl*-2-*methoxy-naphthalene* crystallised from petroleum ether in white lustrous soft needles, m.p. 68–69° C. (Found: C, 81·9; H, 10·3; $C_{27}H_{40}O_2$ requires C, 81·8; H, 10·1 per cent.)

1-*Hexadecyl*-2-*naphthol* prepared by the clemmenson reduction was crystallised from alcohol in white small plates m.p. 70–71° C. (Found: C, 84·2; H, 10·8; $C_{28}H_{40}O$ requires C, 84·4; H, 10·9 per cent.)

2-*Methyl*-3-*tetradecyl*-1 : 4-*β-naphthapyrone* was crystallised from alcohol in small, white, lustrous needles, m.p. 73–74° C. It was soluble in usual organic solvents and its solution in concentrated sulphuric acid gave brownish-yellow colouration. (Found: C, 82·9; H, 9·2; $C_{28}H_{36}O_2$ requires C, 82·8; H, 9·4 per cent.) The chromone on hydrolysis with dilute alkali gave the original ketone.

Ethyl-1-*palmityl-β-naphthoxy acetate* was obtained from the ketone and ethyl brom-acetate as a yellow, oily liquid, b.p. 263° C. (Found: C, 76·8; H, 9·7; $C_{30}H_{44}O_4$ requires C, 76·9; H, 9·5 per cent.)

1-*Palmityl-β-naphthoxy-acetic acid* prepared by the hydrolysis of ethyl-1-palmityl-β-naphthoxy acetate by alkali was crystallised from alcohol in white lustrous plates, m.p. 64–65° C. (Found: C, 76·5; H, 9·1; $C_{28}H_{40}O_4$ requires C, 76·3; H, 9·2 per cent.)

The p-*nitrophenylhydrazone* of the 1-palmityl-β-naphthoxy acetic acid was obtained from alcohol in red, lustrous, small flakes, m.p. 210–11° C. (Found: N, 7·1; $C_{34}H_{45}O_5N_3$ requires N, 7·3 per cent.)

2-*carbethoxy*-3-*pentadecyl-β-naphtha coumarone* prepared from ethyl-1-palmityl-β-naphthoxy acetate and sodium ethoxide was a colourless oily liquid b.p. 245° C. (Found: C, 80·2; H, 9·3; $C_{30}H_{42}O_3$ requires C, 80·0; H, 9·4 per cent.)

2-*Carboxy*-3-*pentadecyl-β-naphtha coumarone* obtained by the hydrolysis of 2-carbethoxy-3-pentadecyl-β-naphtha coumarone, was crystallised from petroleum ether in white plates, m.p. 56–57° C. (Found: C, 79·7; H, 9·3; $C_{23}H_{38}O_3$ requires C, 79·6; H, 9·1 per cent.)

3-*Pentadecyl-β-naphtha-coumarone* prepared by decarboxylating the above acid was crystallised from petroleum ether in white lustrous, small plates,

m.p. 45·46° C. (Found: C, 85·8; H, 10·3; $C_{27}H_{36}O$ requires C, 85·7; H, 10·1 per cent.)

1-*Lauryl*-2-*naphthol* prepared from β-naphthol (7 g.) lauric acid (14 g.) and zinc chloride (7 g.) crystallised from alcohol in white, lustrous flakes, m.p. 95–96° C. It was soluble in usual organic solvents (yield 25 per cent.). (Found: C, 80·7; H, 9·3. $C_{22}H_{30}O_2$ requires C, 80·9; H, 9·2 per cent.)

The p-*nitrophenylhydrazone* of the ketone crystallised from alcohol in yellowish-red, small needles m.p. 165–66° C. (Found: N, 9·0; $C_{28}H_{35}O_3N_3$ requires N, 9·1 per cent.)

1-*Lauryl*-2-*methoxy-naphthalene* crystallised from petroleum ether in white, flat needles, m.p. 54·55° C. (Found: C, 81·3; H, 9·6; $C_{23}H_{32}O_2$ requires C, 81·2; H, 9·4 per cent.)

1-*Dodecyl*-2-*naphthol* crystallised from alcohol in white lustrous, small plates, m.p. 65–66° C. (Found: C, 84·4; H, 10·2; $C_{22}H_{32}O$ requires C, 84·5; H, 10·3 per cent.)

2-*Methyl*-3-*decyl*-1 : 4-β-*naphthapyrone* crystallised from alcohol in white shining small flakes, m.p. 69–70°C. Its solution in concentrated sulphuric acid gave brownish-yellow colouration. (Found: C, 82·4; H, 8·5; $C_{24}H_{30}O_2$ requires C, 82·2; H, 8·6 per cent.) The pyrone on alkaline hydrolysis gave the original ketone.

Ethyl-1-*lauryl*-β-*naphthoxy-acetate* was obtained as a straw-yellow, oily liquid, b.p. 230° C., from ethyl brom-acetate and 1-lauryl-2-naphthol. (Found: C, 75·9; H, 8·7; $C_{26}H_{36}O_4$ requires C, 75·7; H, 8·8 per cent.)

1-*Lauryl*-β-*naphthoxy-acetic acid* crystallised from alcohol in white, shining plates, m.p. 47–48° C. (Found: C, 74·8; H, 8·6; $C_{24}H_{32}O_4$ requires C, 74·9; H, 8·4 per cent.)

The p-*nitrophenyl hydrazone* of the above naphthoxy acid crystallised from alcohol in red plates, m.p. 200-01° C. (Found: N, 8·3; $C_{30}H_{37}O_5N_3$ requires N, 8·1 per cent.)

2-*Carbethoxy*-3-*undecyl*-β-*naphtha coumarone* was obtained as a colourless oily liquid, b.p. 215° C., by the action of sodium ethoxide on ethyl-1-lauryl-β-naphthoxy acetate. (Found: C, 79·2; H, 3·5; $C_{26}H_{34}O_3$ requires C, 79·1; H, 8·7 per cent.)

2-*Carboxy*-3-*undecyl*-β-*naphtha-coumarone* crystallised from petroleum ether in white small plates, m.p. 42–43° C. (Found: C, 78·8; H, 8·3; $C_{24}H_{33}O_3$ requires C, 78·7; H, 8·2 per cent.)

3-*Undecyl-β-naphtha coumarone* was crystallised from hexane in white, lustrous plates, m.p. 36–37° C. (Found: C, 85·6; H, 9·5; $C_{23}H_{30}O$ requires C, 85·7; H, 9·4 per cent.)

We express our grateful thanks to Rev. Father A. M. Coyne, S.J. and late Prof. R. N. Bhagvat, M.A., B.Sc., for their kind interest and provision of the facilities.

Summary

1-Stearyl, 1-palmityl, and 1-lauryl-2-naphthols have been prepared by the Nencki process. These hydroxy ketones were methylated, and reduced by Clemmensen's method. They were subjected to the Kostanecki reaction, and condensed with ethyl bromacetate, to obtain the chromones and coumarones containing these long-chain alkyl groups.

A CHEMICAL AND PETROLOGICAL STUDY OF SOME DYKE ROCKS IN THE PRE-CAMBRIAN (CUDDAPAH TRAPS)*

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Introduction

The suite of traps that forms the subject of this paper occurs as intrusions in the Vempalle limestones and the Tadpatri shales of the Lower Cuddapahs in the Pulivendla taluk of Cuddapah, the Tadpatri taluk of Anantapur and the Dhone taluk of Kurnool. They were collected from a large area in the Cuddapah basin extending from Betamcherla in the Kurnool district to near Vempalle in the Cuddapah district, so that they are representative of the numerous sills that traverse the area. The collection includes also two or three specimens of trap rocks intrusive into the Archaean gneisses near Tiruttani in the Chittoor district. Judging from petrological characters the Tiruttani rocks are probably of the same age as that of the Cuddapah traps, but we have no stratigraphical data to determine the relationship between these two.

These traps form numerous sills and are occasionally lenticular though generally regular and of uniform thickness. The thicker sills often contain intercalations of Vempalle limestones or Tadpatri shales. They are fine-grained and of uniform grain, being composed generally of labradorite feldspar, augite and micropegmatite with subordinate biotite, magnetite, epidote, glass and secondary alteration products. It is only rarely that they exhibit any difference in the grain-size between the centre and the margins. Such a sill, composite in nature, is seen passing through Pulivendla as noted by Dr. C. S. Fox. The central portion of the sill is very basic and contains coarse grains of abundant olivine, augite, enstatite, serpentine, a little feldspar, iron ore and brown mica and thus differs from the layers above and below it, which are dolerites without olivine. The trap sills are fairly conspicuous because of their forming dark low ridges which are marked by brown coloured soil and thorny shrubs. In some places the rocks show the presence of amygdaloidal cavities filled up with secondary infillings and

* Thesis (abridged) approved by the Madras University for the M.Sc. degree and published with their permission.

are also traversed by veins of epidote which shows up well because of its marked green colour.

The Cuddapah traps have not been studied by any one so far in any detail. As early as 1890, P. Lake described briefly the olivine-bearing traps of Juturu. Subsequently (Sir) T. H. Holland (1897 B) classified "some dykes of basic igneous rocks which break through the 'pyroxene granulites' and which he regarded as the dyke-representative of the Cuddapah lava flows" and gave a mineralogical description of these rocks. More recently (Sir) C. S. Fox (quoted by A. L. Coulson, 1934) and A. L. Coulson (1933, 1934) have referred to these traps only incidentally in their description of asbestos and barytes occurrences in the Cuddapah formations. No chemical data are available except for the two modern analyses given by A. L. Coulson in his memoir on asbestos (1934) and the two much earlier analyses given by Holland in 1897.

In the following pages are described the petrographic and chemical characters of these trap rocks. The chemical analyses were done in the Geology Department of the Presidency College, Madras. The analytical results are subjected to the petrochemical studies introduced by Prof. Dr. P. Niggli of Zürich. The plagioclase feldspars and pyroxenes have been studied by the Universal Stage methods, which include the twinning laws and other optical characters. The textural relationship exhibited by the rocks has also been studied in detail, which showed that these minerals have crystallised simultaneously to a large extent.

It has been possible from these studies to trace the chemical characters of these traps, the trends of differentiation of the magma in the evolution of the various types, and the sequence of crystallisation of these traps in the differentiation history. The general results show that the magma which gave rise to the Cuddapah traps is of calc-alkali or tholeiite type. The Cuddapah traps are similar in many respects to the 'Newer dolerites' of Singhbhum, Keonjhar and other areas in the Iron ore series of Orissa and Singhbhum. They are also similar to the Gwalior traps in the nature of their pyroxenes, but are lower in alkalis and higher in alumina. They differ from the Deccan traps, the Karroo dolerites, the Tertiary dykes of the Island of Mull, the Whin Sill and the Palisades diabase in containing no pigeonite.

Mineralogy

Although uniform in their mineralogical characters and chemical composition the trap rocks under study may be divided into three textural groups.

1. *Fine-grained variety.*—This varies from dolerite to basalt and is usually dark in colour, compact and also highly vesicular.

2. *Medium-grained variety.*—This type is mostly black to dark-grey in colour and is represented by quartz dolerite.

3. *Coarse-grained variety.*—This type, formed by the slow cooling of the magma is found to occupy mostly the middle portions of the dykes or sills. It includes olivine dolerites and quartz dolerites.

The grain-size of the minerals composing the rock varies on the average from 0·2 mm. to 0·5 mm. in the fine-grained varieties, and 0·5 mm. to 1 mm. in the medium-grained rocks, to more than 1 mm. in the coarse-grained types. The petrological characters of the various specimens collected are fairly uniform, but some of the vesicular basalts differ from the normal types in containing much palagonite, often to the exclusion of pyroxene.

Microscopic characters.—One striking feature observed under the microscope is the relationship between feldspar and pyroxene. Small laths of feldspar are enclosed either partly or wholly in elongate or stumpy prisms of augite or the augite may be developed in irregular form in the interstices of the penetrating plagioclase laths. Besides this marked doleritic and sub-ophitic development of plagioclase and augite, ophitic, inter-granular and intersertal textures are also noticed. In the olivine-bearing types, olivine is enclosed by large prismatic crystals of pyroxene. Micropegmatite and quartz occur occasionally in the interstices of the feldspars and augites. In the fine-grained types these are represented by a vague mesostasis of weakly refracting glass with grains of opaque magnetite and imperfectly developed microlites of feldspar. Generally the magnetite is distributed evenly throughout the rock. Biotite and hornblende occur as alteration products. Apatite and specks of pyrite are the usual accessories. The rocks have been subjected to secondary alteration such as palagonitisation, sericitisation, serpentinisation and kaolinisation.

The vesicular and amygdaloidal basalts have their vesicles filled up by palagonite and calcite and occasionally also by quartz instead.

In the following paragraphs the feldspars, pyroxenes, micropegmatite and other minor constituents are described.

Plagioclase.—Plagioclase is the dominant constituent of all the normal rocks examined, except in the olivine-bearing type in which it is subordinate in amount to olivine and pyroxene. Megascopically the feldspars are bluish to dark-grey in colour. The crystals exhibit generally polysynthetic twinning,

but simple twinning is also met with and occasionally untwinned plagioclase laths are found in association with quartz pieces.

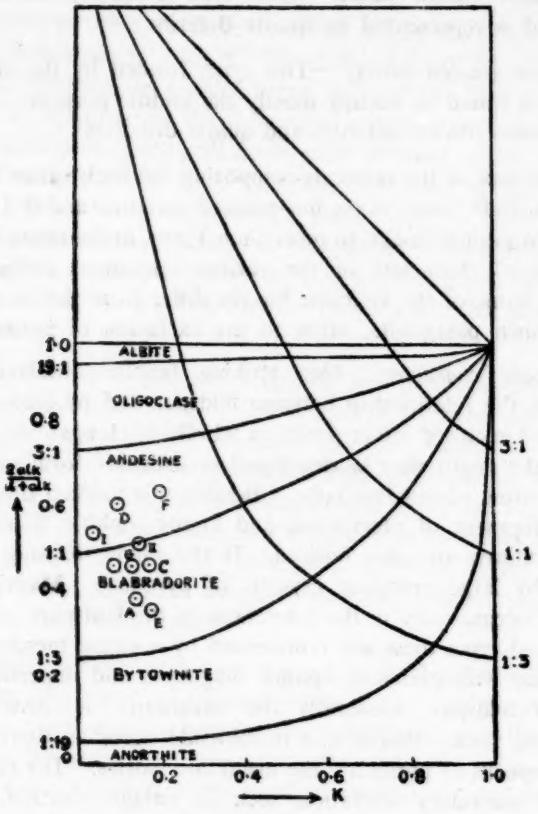


FIG. 1

$k - \frac{2\ alk}{al + alk}$ diagram for the Cuddapah Traps

The composition of the plagioclase feldspars and the twinning law obeyed by them were determined on the Federov Universal Stage. The anorthite content of the feldspars is found to vary from 75 to 30 per cent. Zoning is developed rather inconspicuously in most of the larger laths, being represented by a slight variation in the extinction angle towards the interior. In some cases, however, prominent zoning is observed, the composition passing from labradorite with about 60 per cent. anorthite to a thin external layer of andesine or oligoclase. The average composition of the plagioclase

is deduced to be near about 55 per cent. anorthite and the first plagioclast to crystallise from the melt of this composition would contain about 75 per cent. anorthite. The feldspar phenocrysts found in the vesicular basalet (Type D, which is described later) do not show any marked zoning, the composition of these and of the groundmass feldspars being more or less the same. It is porbable, therefore, that the early formed plagioclase has been 'made over' to the composition of the later feldspars with the result that zoning has disappeared. The plagioclases exhibit predominantly twinning on (010) as the composition plane of different lamellæ with Albite and Carlsbad laws occurring frequently.

The composition of plagioclase can also be deduced from the chemical analysis of the rock, if the calculated k and $\frac{2alk}{al+alk}$ values (Table V) are plotted in Niggli's diagram (Fig. 1). It will be seen from the diagram that the nature of plagioclase deduced from the chemical composition of the rock agrees fairly well with optical determinations. It may be pointed out that the average falls close to 55 per cent. anorthite which is also the average arrived at from optical investigations. A and E have a higher anorthite content than the rest, but from the description of these rocks given elsewhere it will be seen that A is a highly basic rock belonging definitely to an earlier period in the history of consolidation, while E, if not so very basic, is highly feldspathic and also altered, which is reflected in the higher anorthite content of the rock.

Pyroxene.—The pyroxenes are found to belong mostly to the monoclinic variety. In the olivine-bearing types, however, rhombic pyroxenes were also noted in addition. The monoclinic pyroxene is usually augite with large optic axial angle; the other variety of monoclinic pyroxene, pigeonite with small optic axial angle was not detected in any of the analysed specimens but was present in slide No. 8 (1 mile east of Vemula) in small amount.

The monoclinic pyroxene is generally colourless in thin sections, but shows a slightly yellowish or greenish tinge; some grains are also pinkish, indicating that they are titaniferous. The mineral occurs in elongated or stumpy prisms generally twinned on (100) showing sometimes salite and herringbone structures. It may also be irregular in shape, with two sets of cleavage. The optic axial angle varies from 40° to 56° and $Z \wedge C$ from 36° to 46°.

In the olivine-bearing types the rhombic pyroxene occurs in irregular form, intergrown with olivine and monoclinic pyroxene and is colourless.

The optic axial angle (negative) in the plane parallel to (010) varies from 79° to 85°. From this value a composition of En_{81} Fs_{19} is deduced from Burri's diagram (p. 181, 1941) for the rhombic pyroxene.

Comparative study of the py oxenes found in this ancient intrusive rock with those in the basic rocks from India and from other parts of the world is interesting. Dr. L. A. N. Iyer (1932) who investigated the 'Newer dolerites' of Bihar and Orissa found that the pyroxenes in them have a larger optic axial angle, varying from 56° to 68° but has not recorded any pyroxene of small optic axial angle. Dr. M. S. Krishnan (1936) in his studies of the 'Newer dolerites' of Keonjhar State, Bihar and Orissa, did not report the presence of pigeonite in the dolerites and basalts, whereas in the norite dykes he was able to distinguish pyroxenes of small optic axial angle. In his paper on the Gwalior traps M. P. Bajpai (1935) has not reported the optic axial angles of augites seen in the slides. P. R. J. Naidu* found that the 'abnormal' dolerite dykes cutting the charnockite areas of Halagur and Dodkanya, Mysore, contain pigeonite. The pyroxenes of the Deccan traps have generally a small optic axial angle and belong to the pigeonite group as pointed by H. S. Washington (1922) and L. L. Fermor (1925). The Whin Sill (Holmes and Harwood, 1928), the Karroo dolerites (Daly and Barth, 1930, and Walker and Poldervaart, 1940) and the New Jersey diabases (Walker, 1940) exhibit characters similar to each other in having all the three pyroxenes—hypersthene, augite and pigeonite. In all these cases, there is a complementary relationship between hypersthene and pigeonite. In his latest paper on the 'Pyroxenes of common mafic magmas' H. H. Hess (1941) has come to the interesting conclusion that the complementary relationship is due to the inversion of the lime-poor ortho-pyroxene to pigeonite at En_{70} Fs_{30}, so that for any ratio less than 7:3, pigeonite takes the place of the ortho-pyroxene.

This study shows that the Cuddapah traps contain predominantly monoclinic pyroxenes with large optic axial angle. The dolerites of later ages appear to contain all the three pyroxenes, pigeonite being dominant in the normal Deccan traps. In view of the nature of the pyroxenes in these rocks, it would be pertinent to compare the normative composition and the metasilicate proportion of pyroxene, calculated from the average chemical composition with those of other rocks and see how this important difference can be accounted for (see Table I). The diopside and hypersthene molecules of the average Cuddapah traps and 'Newer dolerites' are similar except

* *Current Science*, 1943, 12, 115.

for a slightly higher content of these in the latter. The Karroo dolerites are also similar to the above dolerites in their containing more hypersthene than diopside. But, in contrast to this, the Deccan trap shows equal amounts of both these molecules. The Whin Sill, though containing more hypersthene than diopside, shows less of both these molecules than the other rocks.

TABLE I

The normative composition of Pyroxenes in the Cuddapah traps and other dolerites and basalts

	Di	Hy	$CaSiO_3$	$MgSiO_3$	$FeSiO_3$
A	8·90	20·91	14·5	67·8	17·7
B	13·82	13·74	24·8	50·0	25·2
C	16·36	25·27	19·6	44·3	36·1
D	2·26	24·26	..	..	..
E	12·36	23·09	17·1	60·0	22·9
F	17·16	14·56	26·9	43·8	29·3
G	21·24	17·12	27·5	44·1	28·4
I	16·45	20·80	21·9	47·7	30·4
II	17·54	21·22	22·6	41·8	35·6
III	17·41	17·78	24·6	44·3	31·1
IV	16·76	25·74	19·6	46·6	33·8
V	13·14	15·90	22·3	52·3	25·4
VI	14·71	21·08	20·3	53·9	25·8

A to G. Cuddapah traps.

I. Average of 8 analyses of Cuddapah traps.

II. Newer dolerite. Average of 3 analyses of Newer dolerites, Singhbhum (L. A. N. Iyer, 1932) and 2 of Keonjhar State (M. S. Krishnan, 1936).

III. Average of 11 analyses of Deccan traps (H. S. Washington, 1922).

IV. Average of 5 analyses of Karroo dolerites (Daly and Barth, 1930).

V. Average of 6 analyses of Whin Sill (Holmes and Harwood, 1928).

VI. Average New Jersey basalt (Anderson, 1940).

The metasilicates in the averages of these rocks are remarkably uniform in showing a lower proportion of $CaSiO_3$ and higher proportion of $MgSiO_3$, while $FeSiO_3$ is intermediate between these values. On a careful scrutiny it would appear that there is a reciprocal relationship between $MgSiO_3$ and $FeSiO_3$, for a decrease in $MgSiO_3$ results in the increase of $FeSiO_3$ but such a notable change is not observed in $CaSiO_3$. The explanation for this can be had from Fig. 2 which shows that pyroxenes of mafic magmas become enriched in iron and correspondingly impoverished in magnesium.

Thus, in view of the absence of any marked difference in the normative composition of the pyroxenes of the various rocks compared with the Cuddapah dolerites, the metasilicate proportions of the rocks analysed were plotted in the above figure. All except type A fall above the cotectic line.

This type is rich in olivine and carries rhombic pyroxene. A study of the thin section goes to show that the rhombic pyroxene was the first to crystallise. The clino-pyroxene joined later and both crystallised out before the rhombic

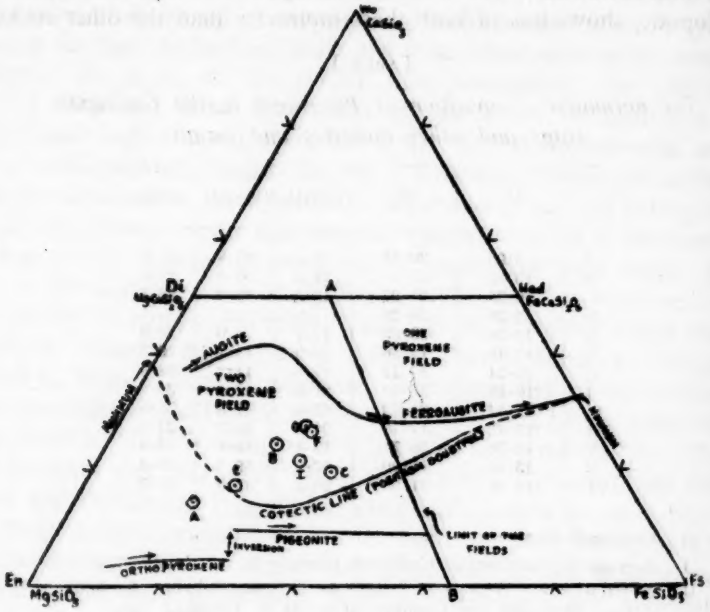


FIG. 2

The trend of crystallisation of pyroxenes from mafic magmas (After H. H Hess)

pyroxene reached the composition En_{70} Fs_{30}. In all the other rocks only one pyroxene was distinguished and the points for these rocks lie above the cotectic line. To account for the presence of only one pyroxene it could be reasonably supposed that the degree of reaction obtained between the melt and the crystals suspended in it was such that the melt never reached the cotectic line and this process might have been greatly assisted by the volatile constituents of the magma.

Pyroxene-Feldspar Relations and the Order of Crystallisation

To describe the different types of textural features in relation to the pyroxenes and feldspars various names have been proposed by different writers. Krokström (1933) has proposed four names, namely, ophitic, sub-ophitic, doleritic and sub-doleritic. The ophitic and sub-ophitic textures in basaltic rocks indicate that the feldspars are of earlier crystallisation while

the doleritic and sub-doleritic textures point to the simultaneous crystallisation of these minerals.

In the Cuddapah traps, the pyroxenes are generally larger in size than the plagioclases. The shapes of these pyroxenes are to a great extent determined by those of the adjacent feldspar laths. Sometimes the pyroxenes are also sub-idiomorphic with a roughly prismatic habit. Besides these, in some slides ophitic and sub-ophitic textures in the restricted sense of Krokström are also found, the pyroxenes then filling narrow interstices between two neighbouring feldspars, and different pieces over wide areas showing simultaneous extinction, with similar orientation or optical continuity. The pyroxenes also enclose completely numerous small laths of plagioclase showing that they are definitely later than the plagioclase in crystallisation.

Barth (1936) has discussed the crystallisation process of basalt and suggested that the initial composition of the magma determines whether pyroxene or plagioclase is the first mineral to crystallise. When crystallisation of the first mineral is going on, the melt moves towards the boundary surface where simultaneous crystallisation of both minerals would take place. Barth has deduced, from a study of the plateau-basalts which show unequivocally simultaneous crystallisation of pyroxene and plagioclase, this boundary surface in a tetrahedron with the normative minerals *ab*, *an*, *di* and *hy* at the corners. The position of the boundary surface is got from the sum of $ab' + 2\,di' + 2{\cdot}3\,hy'$, which is called the *f* (*norm*). If the *f* (*norm*) is near about 123 the basalt falls on or near about the boundary surface and simultaneous crystallisation is to be expected. If the *norm* is smaller or greater than 123 the basalt lies in the plagioclase field or in the pyroxene field respectively. The *f* (*norm*) values for the Cuddapah traps and for the other basalts compared with them are given in Table II.

It will be seen from Table II that the *f* (*norm*) is around 123 for all types except A, B and E which have a higher or lower value. Type A is a rock of ultrabasic composition and from an examination of the thin section it is clearly seen that olivine and pyroxene are earlier than the plagioclase which is subordinate in amount and occupies the interstices between these minerals. In the rock designated B the pyroxenes are intergranular and intersertal to the feldspars which penetrate the former so that we can conclude that the feldspars crystallised earlier. The high percentage of alumina in this rock results in an excess of feldspar which causes crystallisation in the feldspar field itself. As has already been mentioned, the rock E shows high alumina percentage and the feldspars are extensively kaolinised so that the high per-

TABLE II

f (norm) for Cuddapah and other traps

	ab'	*an'*	*di'*	*hy'*	*f* (norm)
A	16·6	30·9	15·7	36·8	132·6
B	28·0	37·7	17·2	17·1	101·7
C	21·2	30·8	18·9	29·1	125·9
D	..	..	..	..	..
E	18·0	42·8	13·7	25·5	104·1
F	34·0	24·0	22·7	19·3	123·8
G	23·8	32·5	24·2	19·5	117·0
I	30·2	27·3	42·1	0·4	115·3
II	24·6	28·1	16·8	30·5	128·4
III	26·2	30·4	19·2	24·2	120·3
IV	27	29	22	22	122
V	29·3	25·6	20·4	24·7	126·9
VI	27·9	32·3	18·0	21·8	114·0
VII	20·5	32·5	20·5	26·5	122·5
VIII	29·2	28·3	17·4	25·1	121·7

A to II. Cuddapah traps.
III. Average of B to II.
IV. Average of 11 analyses of Deccan traps (Washington, 1922). As given by Barth (1936), Tab. 3, p. 332.
V. Newer dolerite. Average of 3 from Singhbhum (L. A. N. Iyer, 1932) and of 2 from Keonjhar State (M. S. Krishnan, 1936).
VI. Whin Sill. Average of 6 analyses by Harwood (Holmes and Harwood, 1928).
VII. Karroo dolerite. Average of 4 analyses (Daly and Barth, 1930). As given by Barth (1936), Tab. 3, p. 332.
VIII. Average New Jersey basalt (Anderson, 1940).

centage of alumina may partly be due to alteration. But from the nature of the rock it can be said that even though some feldspars may have been precipitated first the bulk of them crystallised approximately simultaneously with the pyroxenes.

From these studies we can conclude that during the earlier stages of crystallisation—excepting in type A—the feldspars crystallised to begin with, but were very soon joined by the pyroxenes so that in all the normal types the two minerals have crystallised simultaneously.

Micropegmatite.—There is some acid material in these basic dykes in the form of micropegmatite, quartz and acid glass, which are found in the interstices, forming a mesostasis to the earlier formed feldspars and pyroxenes; sometimes they may also form megascopic patches.

This acid material is considered by most petrologists as the last phase in the consolidation of the magma. It is present in many basic rocks in India and elsewhere. As early as 1897, Holland discussed the origin of

micropegmatite in the basic dykes of the Madras Presidency including those of Cuddapah age and concluded that the micropegmatite "is really original, the last phase in the consolidation of the rock" (p. 34, 1897 A).

Bowen (pp. 70-74, 1928) considers that quartz or acid residue in basic rocks is due to the early separation of olivine in excess of its stoichiometric proportion. But Fenner (1929 and 1931) objects to this theory on the ground that the earlier ferromagnesian silicates contain an excess of magnesia, while the residual liquid gets enriched in iron so that magnetite, pyroxene and feldspar crystallise during final stages. So he concludes that micropegmatite does not normally result from the process of crystallisation-differentiation, but is a secondary product of hydrothermal activity after the rock has completely solidified. Kennedy (1933) advocates two distinct types of basaltic magmas, *viz.*, tholeiitic and olivine-basaltic types, and considers that the tholeiitic magma, represented by most plateau-basalts gives rise, on differentiation, to a liquid of acid composition and that the olivine-basalt (oceanic basalt) magma gives rise always to a liquid of feldspathoidal composition poor in quartz. The Cuddapah trap would fall under the tholeiitic type as will also be pointed out later. The tholeiitic type does not seem to have any significance in space and geological time as it is found in various ages in both fissure and central eruptions.

Minor Constituents

The other constituents seen in these rocks are biotite, amphibole, glass, chlorite, magnetite, hematite, epidote and clino-zoisite, apatite and pyrite with such secondary products as sericite, kaolin and calcite. A short description of the more important of these is given below.

Glass.—In all the fine-grained types the glass forms a mesostasis to the main constituents. It is colourless, light brown or dark in appearance and in almost all cases wholly devitrified, containing acicular crystals and microlites as also small rounded grains of magnetite.

Chlorite.—Both penninite and delessite are distinguishable. Penninite is greenish or bluish green in colour and weakly birefringent with 'ultra blue' interference colours. Delessite occurs in fibrous sheaves with positive elongation of the fibres, straight extinction and low birefringence. It is pleochroic according to the general scheme:

$$Z = Y = \text{Green}; \quad X = \text{Straw yellow}$$

Iron ores.—Magnetite is found in all the rocks as an accessory mineral. It is in the form of large grains, sometimes with crystal contours and sometimes in granular clusters. The great part of this mineral is of an earl

generation, but in some cases evidence of late crystallisation is also found. The presence of leucoxenic material in some of the sections shows that part of it may be titaniferous.

Epidote and Clinozoisite.—The epidote aggregates consist of minute grains recognised by their high refringence and birefringence. They are strongly pleochronic, from very pale green to yellowish green. The clinozoisite is colourless to pale green and similar to epidote but shows very low birefringence. It forms granular aggregates mostly derived from the alteration of feldspars.

Petrographical Description and Chemical Analyses of the Cuddapah Traps

Seven representative specimens of traps from different localities in th area were chosen for chemical analyses so as to cover the general types encountered. The analytical results and norms are given in Table III. The rocks are arranged in the order of increasing silica percentage but not necessarily in the order of increasing acidity as represented by saturation. The analysed types are briefly described below.

A. *Picrite* (Hornblendeperidotitisch).—The rock is coarse-grained and dark in colour and is very largely made up of olivine and pyroxene. Olivine (0·2–0·9 mm.) is colourless and mostly rounded in appearance with characteristic ' mesh ' structure having an optic axial angle (2V) of + 84° to + 88°. Both ortho-pyroxene and clino-pyroxene are encountered. The ortho-pyroxene is enstatite occurring as large individuals (1 to 2·1 mm.) of irregular shape. The interference colours are 1st order grey to white and the optic axial angle (2V) in the plane perpendicular to *b*-axis is − 82° to − 84°. The clino-pyroxene (1 to 2·3 mm.) is intergrown with ortho-pyroxene and is mostly colourless, often with a yellowish tinge. The optic axial angle is about + 50° to + 55° while the angle $Z \wedge C$ varies from 36° to 38°.

The plagioclase which is subordinate in amount is largely altered and could not be determined, though showing broad lamellæ. From Niggli's diagram and from the norm, the composition is deduced to be 62 per cent. anorthite.

There are, in addition, alteration products, such as magnetite, serpentine, brown mica, sericite, kaolin and chlorite.

The mode of the rock is given below:

Olivine	34·3	Chlorite and serpentine ..	17·9
Pyroxene (ortho & clino) ..	20·3	Biotite	4·4
Plagioclase	18·6	Magnetite	4·3

When the mode is compared with the norm, it will be seen that the amount of olivine actually present in the rock is less than the normative amount. The pyroxene and feldspar are also less than the normative percentages. But the modal magnetite is higher. Chlorite, serpentine and biotite make up this deficiency between the mode and the norm.

B. *Pyroxene dolerite* (Normalgabbroid, *c*-gabbroid).—This rock is medium-grained and compact and bluish to dark-grey in colour and is made up of bluish plagioclase, dark dull pyroxenes and magnetite. The plagioclase is seen in small slender laths (0·2 by 0·8 mm.) developed in sub-ophitic relationship to pyroxenes. The feldspar is mostly labradorite with an anorthite content of 60 to 70 per cent.

The augite is always irregular in shape and faintly pinkish in colour with very weak pleochroism in yellowish or greenish tinges. The optic axial angle varies from $+41°$ to $+45°$ while the angle $Z \wedge C$ varies from 39° to 43°.

Chlorite, magnetite and sericite and kaolin occur as alteration products. Apatite is rarely found.

The mode of the rock is as follows:

Plagioclase	44·2	Magnetite	9·2
Pyroxene	22·5	Sericite	5·5
Chlorite	18·8		

When the mode is compared with the norm it is seen that the amounts of feldspar and pyroxene are lower in the mode than in the norm. This we can expect from the alteration of the minerals.

C. *Dolerite* (normalgabbroid; *c*-gabbroid).—The rock is dark-grey in colour, composed of greyish feldspars, dark ferromagnesians and a few pieces of magnetite. The plagioclase feldspars make up the bulk of the groundmass in the form of small laths (0·15 to 1·4 mm.) developed in sub-ophitic relationship to the pyroxenes which they penetrate from the edges and make the pyroxenes angular. A composition of about 55 per cent. anorthite is deduced from both Niggli's diagram and the norm. They could not be determined on account of the alteration suffered by them.

The augite is colourless, occurring as large crystals twinned on (100) and encloses small laths of twinned plagioclase in addition to showing a marked doleritic structure. The optic axial angle (2V) in the plane parallel to (010) varies from $+44°$ to $+47°$ while $Z \wedge C$ in the same plane is 40° to 42·5°.

Micropegmatite and quartz pieces are also seen in the slide. As secondary minerals, magnetite, chlorite, kaolin, sericite and calcite are seen.

D. *Vesicular basalt-porphyry* (Natronlamprosyenitisch).—This is a dark-coloured rock with porphyritic crystals of feldspar embedded in a groundmass of chlorite and small feldspars of the same character. The rock is highly vesicular and the vesicles are filled up by dark, friable, chloritic material which has a dirty-green colour. Inclusions of calcite and a dark-green or yellowish green mineral, not scratched by pen-knife, are seen in the chlorite.

The porphyritic plagioclases twinned according to Albite-Ala and Ala (Es) are found either as rectangular tables or as thick elongated prisms. The groundmass plagioclases are in the form of small laths and exhibit twinning after the same laws. The composition is 33 to 40 per cent. anorthite.

Clinozoisite and calcite are found associated with chlorite as they are the result of the alteration of feldspar. Clinozoisite, embedded in palagonite, is twinned on (100) showing the characteristic section of crystals of monoclinic symmetry. The extinction angle with reference to *c*-axis varies from 4° to 8°.

E. *Quartz-dolerite* (Miharaitisch).—This is a medium-grained rock composed of greyish plagioclase and dark ferromagnesian minerals.

Plagioclase is the most abundant mineral in the rock, giving lath-shaped sections. It is usually much altered to kaolin and sericite.

The pyroxenes, often twinned on orthopinacoid, are irregularly shaped and sometimes prismatic and short. They are pale greyish yellow to colourless. The optic axial angle ($+2V$) in the plane parallel to (010) is from 52° to 56°. The angle between the axis of minimum elasticity and the vertical crystallographic axis is about 39°. Some of the pyroxenes are altered to serpentine.

Quartz and micropegmatite are intergrown with the feldspars. Some of the quartz may be of secondary origin on account of kaolinisation of feldspars. The minor constituents are magnetite, biotite and chlorite.

F. *Fine-grained Basalt* (Melagabbrodioritisch).—This is a fine-grained cryptocrystalline dark-coloured rock composed of minerals indistinguishable even with the help of a good pocket lens. The rock is merocrystalline under the microscope with imperfectly developed microlites of plagioclase embedded in a mosaic of pyroxene, palagonite and glass. Twinning is imperfectly developed. The composition is deduced as 39 per cent. anorthite from Niggli's diagram. The pyroxenes are seen as small rounded or rectangular,

pale yellow to colourless pieces with a tendency to be grouped in aggregates. Some rectangular prisms show simple twinning.

Magnetite occurs as relatively larger grains and enclose feldspars and pyroxenes. They are distinctly later than these minerals in consolidation. A few pieces of dichroic hæmatite are also seen.

The interstices of all these minerals are filled up by palagonite, ill-defined glass and chalcedony. A few pieces of zoisite and calcite are also noticed.

G. *Quartz-dolerite* (Miharaitisch).—This is a medium-grained dark-grey trap composed of grey plagioclase and dark ferromagnesian minerals. It shows two thin veinlets perpendicular to each other, consisting of palagonite which pass from one piece of chlorite or amphibole to another through feldspathic and micropegmatitic portions. It appears to have been formed as veins from magmatic fluids during the late stages of activity.

The plagioclases occur as laths 3 to 7 mm. in length with ill-defined relationship to pyroxene. They show twinning after Albite, Carlsbad or Albite-Carlsbad law and contain between 54 and 70 per cent. of anorthite. Zoning as well as secondary alterations are observed.

The augite is colourless and non-pleochroic often exhibiting simple twinning on the orthopinacoid. The optic axial angle is $+49{\cdot}5°$ and $Z \wedge C$ is 46°.

Micropegmatite generally fills the interspaces between pyroxenes and feldspars and is composed of quartz and feldspar, intergrown micrographically. The quartz carries inclusions of bluish crystals, probably apatite and numerous minute dark inclusions.

As secondary alteration products, hornblende, biotite, iron ore and chlorite are noticed.

The mode of the rock is given below:

Plagioclase	37·6	Chlorite and Amphibole ..	16·9
Micropegmatite ..	8·3	Magnetite	2·5
Pyroxene	33·5	Biotite	1·4

The modal feldspar and pyroxene are less than the normative amounts on account of the alteration of these minerals to secondary products.

General Review of Chemical Composition

Having made a petrographical study of the traps we can proceed to review their general chemical characters and compare them with well-known types such as the plateau-basalts and tholeiites from India and elsewhere.

Considering the analyses A to II (Table III) it is seen that type A is distinctly different from the others. Its silica content is lowest and alumina is less than in the other rocks. The iron-oxides present are about normal to basalts, with ferrous oxide dominating over ferric; magnesia is decidedly high while

TABLE III

Analyses of the Cuddapah Traps

	A	B	C	D	E	F	G	I	II	III
SiO_2 ..	45·28	46·92	48·64	48·95	49·91	50·47	52·02	46·63	50·04	49·20
Al_2O_3 ..	8·64	15·93	14·05	15·09	18·06	12·91	15·18	12·26	13·26	14·59
Fe_2O_3..	1·37	3·82	2·84	5·57	1·18	5·61	2·22	3·84	2·94	3·50
FeO ..	11·10	9·28	11·75	7·69	6·42	9·62	8·32	10·94	12·57	9·57
MnO ..	0·26	0·30	0·34	0·24	0·24	0·27	0·25	0·70	0·83	0·40
MgO ..	21·84	6·85	6·43	6·90	7·96	4·88	5·96	6·46	5·22	6·33
CaO ..	6·11	9·73	9·52	5·72	11·24	8·04	11·11	12·20	8·06	9·45
Na_2O ..	1·08	2·66	2·23	3·69	1·93	3·05	2·46	2·73	2·39	2·64
K_2O ..	0·30	0·36	0·69	0·74	0·66	1·13	0·59	0·16	0·72	0·63
TiO_2 ..	0·44	1·82	1·50	1·09	0·60	1·61	0·73	1·60	1·73	1·34
P_2O_5 ..	0·26	0·23	0·14	0·17	0·27	0·19	0·19	0·19	Trace	0·17
H_2O+	2·80	1·93	1·79	3·25	1·48	2·25	1·17	2·81	1·96	2·08
H_2O-	0·25	0·34	0·43	0·57	0·51	0·44	0·29	0·24	0·31	0·39
	99·73	100·17	100·35	100·03*	100·46	100·47	100·49	100·76	100·03	100·29
Sp. Gr.	3·203	3·939	3·044	3·913	2·983	2·949	2·994	3·137	3·075	3·004
Temp. C	29·5°	29·5°	29·0°	29·5°	29·2°	29·5°	30·75°	..	..	..
					Basis					
Cp ..	0·55	0·29	0·29	0·29	0·56	0·29	0·28	0·29	..	0·29
Kp ..	1·00	1·38	2·43	2·43	2·41	4·21	2·04	0·70	2·47	2·08
Ne ..	5·98	14·85	12·16	20·87	10·44	17·20	13·61	15·33	13·74	14·89
Cal ..	10·47	18·82	16·68	14·09	23·36	11·41	17·53	13·07	14·80	16·27
Cs ..	3·33	5·26	6·17	0·87	4·63	6·58	7·91	12·20	5·29	6·23
Fs ..	1·50	4·14	3·13	6·09	1·35	6·15	2·38	4·18	3·17	3·81
Fa ..	13·13	11·48	14·59	9·57	7·75	12·03	10·13	14·03	16·38	12·02
Fo ..	45·37	14·73	13·98	15·04	16·76	10·71	12·68	14·12	11·45	13·68
Ru ..	0·28	1·32	1·10	0·81	0·45	1·17	0·51	1·16	1·23	0·98
Q ..	18·39	27·70	29·47	29·01	32·29	30·25	32·93	24·92	31·47	29·75
	100·00	100·00	100·00	100·00†	100·00	100·00	100·00	100·00	100·00	100·00
					Kata Norm					
Q ..	..	..	..	..	..	2·69	2·15	..	1·83	..
Or ..	1·67	2·30	4·05	4·05	4·02	7·02	3·40	1·17	4·12	3·47
Ab ..	9·97	24·75	20·27	34·78	17·40	28·67	22·68	25·55	22·90	24·82
An ..	17·45	31·37	27·80	23·48	38·93	19·02	29·22	21·78	24·67	27·12
Wo ..	3·88	4·37	6·03	1·16	5·27	6·43	9·53	13·98	4·59	6·35
Hy ..	5·88	7·24	15·60	8·24	8·88	11·94	11·92	6·44	19·73	12·74
En ..	19·68	11·36	16·90	19·16	20·24	14·28	16·91	7·60	15·30	16·88
Fa ..	7·97	3·98	1·33	0·35	0·42	..	..	7·11	..	0·56
Fo ..	30·61	6·24	1·30	0·66	1·58	..	..	8·42	..	1·02
Tn ..	0·84	3·96	3·30	..	1·35	3·51	1·53	3·48	3·69	2·94
Mt ..	1·50	4·14	3·13	6·09	1·35	6·15	2·38	4·18	3·17	3·81
Ap ..	0·55	0·29	0·29	0·29	0·56	0·29	0·28	0·29	..	0·29
	100·00	100·00	100·00	100·00‡	100·00	100·00	100·00	100·00	100·00	100·00

TABLE III—*Contd.*

	A	B	C	D	E	F	G	I	II	III
				C.I.P.W. Norm						
Q ..	..	..	0·24	0·48	..	3·96	2·82	..	3·18	0·54
Or ..	1·67	2·22	3·89	3·89	3·89	6·67	3·34	1·11	3·89	3·34
Ab ..	9·43	22·53	18·34	31·44	16·24	25·68	20·96	23·06	20·44	22·53
An ..	17·51	30·30	26·69	22·52	38·64	18·07	28·63	20·85	23·35	26·13
Di ..	8·90	13·82	16·36	2·26	12·36	17·16	21·24	32·13	13·98	16·45
Hy ..	20·91	13·74	25·27	24·26	23·09	14·56	17·12	0·33	25·38	20·80
Ol ..	34·82	5·81	..	..	0·62	..	..	11·34	..	..
Il ..	0·76	3·50	2·89	2·13	1·22	3·04	1·37	3·04	3·19	2·58
Mt ..	2·09	5·57	4·18	8·12	1·86	8·12	3·25	5·57	4·18	5·10
Ap ..	0·67	0·34	0·34	0·34	0·67	0·34	0·34	0·34	..	0·34
H_2O ..	3·05	2·27	2·22	3·82	1·99	2·69	1·46	3·05	2·27	2·47
	99·81	100·10	100·42	100·06§	100·58	100·29	100·53	100·82	99·86	100·28

* Total incl ·les 0·36 CO_2. † Total includes 0·93 Cc.

‡ Total includes 0·93 Cc and 0·81 Ru. § Total includes 0·80 of $CaCO_3$.

A. *Picrite* (No. 5) : From the middle of the composite sill near 35 miles 2½ furlongs on the Cuddapah-Pulivendla road. Analyst N. A. Vemban.

B. *Pyroxene dolerite* (No. 30) : 1303 Beduduru Hill (Sheet 57 J/1). Analyst N. A. Vemban.

C. *Dolerite* (No. 9) : From near the village Vemula on the Cuddapah-Pulivendla road. Analyst N. A. Vemban.

D. *Vesicular basalt—Porphry* (No. 46) : 7th mile on the road from Betamcherla to Kalwa. Analyst N. A. Vemban.

E. *Quartz-dolerite* (No. 4) : From upper portion of the still, 35 miles 2½ furlongs on the Cuddapah-Pulivendla road. Analyst N. A. Vemban.

F. *Fine-grained basalt* (No. 49) : Eastern end of Brahmanapalle asbestos zone, Pulivendla taluk, Cuddapah district. Analyst N. A. Vemban.

G. *Quartz-dolerite* (No. 2 *b*) : From the hillock west of Tiruttani, Chittoor district. Analyst N. A. Vemban.

I. *Dolerite* below asbestos zone, Brahmanapalle asbestos mine, Pulivendla taluk, Cuddapah district, *Mem. G.S.I.*, **64**, p. 224, 1934. Analysts P. C. Roy and Mahadeo Ram.

II. *Quartz-dolerite* below asbestos zone, a quarter of a mile south-west of Malkapuram, Dhone taluk, Kurnool district. *Ibid.*

III. Average of 8 analyses of Cuddapah traps B to II.

CaO, alkalis and titania are low. This rock comes under the peridotite-picrite group.

The most striking feature in the series of analyses is the uniformity in composition of the dolerites and basalts with the silica percentage varying from 46·92 to 52·02 per cent. Alumina is present in about the usual amount expected in basalts, except in E which is highly feldspathic. The iron oxides

are usually high except in E and G. Ferrous oxide predominates over the ferric in general but the high ferric oxide content in D and F can be accounted for by the considerable amount of palagonite present. Manganese is low. Compared to the combined iron oxides the amount of MgO is lower. The CaO is about normal. Soda dominates over potash, but in D and F soda is notably higher. Titanium and phosphorus are both in about the normal amounts.

A comparison of the mean analysis of the Cuddapah traps (Table IV) with the average Deccan traps shows that they are closely akin to each other. There is also a close resemblance between the 'Newer dolerites' of Bihar and Orissa and the Cuddapah traps. In comparison, the Gwalior trap contains less alumina and more alkalis. The average analyses of the Karroo dolerites, the Whin Sill and the New Jersey basalts compare closely with that of the Cuddapah traps, as all of them come under the normal tholeiitic types.

PETROCHEMISTRY

For the present study seven analyses of Cuddapah traps were made by the writer and two previous published analyses have been added. This form of expressing the composition (weight percentage of the chief oxides) is not by itself quite suitable for petrographic classification and comparison or for understanding the chemical characters of the rocks and their evolution. For such a study, various new values were calculated by grouping together allied oxides having the molecular proportions of the various oxides as the basis of calculations according to the method of Niggli, which is very helpful in the study of differentiation and of magmatic affinities of rocks. The various calculated values are given in Table V.

Differentiation Trends in the Cuddapah Traps

The rock types under study are all basic in character with the silica content varying from 45 to 52 per cent. (by weight). This small range in silica percentage goes to show that the magma that gave rise to the various types did not undergo extensive differentiation and that most of the rocks represent more or less the composition of the magma itself. Though the silica expressed as weight percentage has a very small range, we can see from the Niggli values that 'si' varies from 81 to 128 units and that there is a well-marked gap of 22 units between si 81 and 103; but there is every gradation from si 103 to 128. This gap is significant for study of the nature and evolution of this magma. In Fig. 3 a generalised differentiation diagram has been drawn from the Niggli values with si as abscissa and the other

TABLE IV

Average Analyses of the Cuddapah Traps and other basic rocks compared with them

	I	II	III	IV	V	VI	VII	VIII
SiO_2 ..	49·20	50·61	52·11	50·18	50·52	52·25	50·66	48·78
Al_2O_3 ..	14·59	13·58	14·35	11·73	13·76	14·60	14·28	15·85
Fe_2O_3 ..	3·50	3·19	1·38	2·02	3·87	0·84	3·41	5·37
FeO ..	9·57	9·92	9·94	11·94	8·50	9·89	8·58	6·34
MnO ..	0·40	0·16	0·18	0·50	0·16	0·45	0·12	0·29
MgO ..	6·33	5·46	5·73	5·45	5·42	6·95	6·92	6·03
CaO ..	9·45	9·45	8·85	10·05	9·09	9·71	8·60	8·91
Na_2O ..	2·64	2·60	2·97	4·47	2·42	2·21	2·92	3·18
K_2O ..	0·63	0·72	1·15	0·95	0·96	0·96	0·72	1·63
TiO_2 ..	1·34	1·91	0·80	1·59	2·39	1·10	1·30	1·39
P_2O_5 ..	0·17	0·39	0·24	0·74	0·26	0·22	0·17	0·47
H_2O+ ..	2·08	1·70	2·08	0·81	1·51	0·71	2·28	1·76
H_2O- ..	0·39	0·43	0·17		0·76	0·32		
	100·29	100·12	99·95	100·43	100·31*	100·21	99·96	100·00
Sp. Gr. :.	3·004	2·916	..	2·98	..	2·990	..	..
si ..	116·8	126·3	131·1	117·6	129·1	126·1	123·6	117·0
al ..	20·4	20·0	21·3	16·2	20·7	20·7	20·5	22·4
fm ..	48·6	47·3	45·6	47·0	46·6	47·6	49·0	44·7
c ..	24·1	25·3	23·8	25·2	25·0	25·0	22·5	22·9
alk ..	6·9	7·4	9·3	11·6	7·7	6·7	8·0	10·0
ti ..	2·4	3·6	1·5	2·8	4·6	2·0	2·3	2·6
p ..	0·14	0·42	0·15	0·73	0·31	0·14	0·15	0·58
k ..	0·12	0·15	0·23	0·12	0·22	0·24	0·13	0·25
mg ..	0·46	0·43	0·47	0·41	0·45	0·53	0·52	0·50

* Total includes 0·58 CO_2 and 0·11 Incl.

I. *c*–gabbroid
II. *c*–gabbroid
III. Normalgabbrodioritisch
IV. Normalgabbrotheralithisch
V. *c*–gabbroid
VI. *c*–gabbroid
VII. Normalgabbroid Normalgabbrodioritisch
VIII. Normalgabbrodioritisch

I. Average of 8 analyses of Cuddapah traps B to II given in Table III.

II. *Deccan Trap :* Average of 11 analyses including I Rajmahal trap. *Bull. Geol. Soc. America*, Vol. 33, p. 774, 1922, Analyst H. S. Washington

III. *Newer dolerite :* Bihar and Orissa. Average of 3 of Singhbhum. *Rec., G.S.I.*, LXV, p. 528, 1932 and 2 of Keonjhar State, *Rec., G.S.I.*, Vol. 71, p. 108, 1936. Analysts L. A. N. Iyer and P. C. Roy.

IV. *Gwalior trap :* Average of 6 analyses. *Jour. Geol.*, XLIII, p. 69, 1935. Analyst M. P. Bajpai.

V. *Whin Sill :* Average of 6 analyses. *Min. Mag.*, XXI, p. 539, 1928. Analyst H. F. Harwood.

VI. *Karroo dolerite :* Average of 5 analyses. *Geol. Mag.*, LXVII, p. 101, 1930. Analysts E. G. Radley and Prior.

VII. *Average New Jersey basalt :* Quoted from C. A. Anderson. *Amer. Jour. Sci.*, 238, p. 486, 1940.

VIII. *Daly's average basalt :* Quoted from Washington, *Bull. Geol. Soc. America*, Vol. 33, p. 797, 1922.

TABLE V

Niggli, QLM and $\pi\gamma$ values of the Cuddapah Traps

	A	B	C	D	E	F	G	I	II
si ..	80·7	107·4	113·4	121·8	115·2	127·6	125·7	102·8	124·1
al ..	9·0	21·4	19·3	22·1	24·5	19·1	21·6	16·0	19·4
fm ..	77·1	48·3	51·0	52·7	42·5	49·9	42·9	49·1	52·4
c ..	11·7	23·8	23·8	15·2	27·7	21·7	28·8	28·8	21·4
alk ..	2·2	6·5	5·9	10·0	5·3	9·3	6·7	6·1	6·8
ti ..	0·53	3·2	2·7	2·1	1·1	3·0	1·3	2·7	3·1
p ..	0·21	0·14	0·14	0·15	0·28	0·15	0·14	0·13	..
k ...	0·14	0·09	0·17	0·10	0·18	0·20	0·13	0·04	0·15
mg ..	0·76	0·49	0·44	0·49	0·65	0·37	0·50	0·44	0·37
Q ..	18·8	28·5	30·2	29·9	32·8	31·0	33·3	25·6	32·1
L ..	17·5	35·0	31·3	37·7	36·2	32·8	33·2	29·1	31·0
M ..	63·7	36·5	38·5	32·4	31·0	36·2	33·5	45·3	36·9
π ..	0·66	0·54	0·53	0·38	0·65	0·35	0·53	0·45	0·48
γ ..	0·05	0·15	0·16	0·03	0·15	0·19	0·24	0·27	0·16

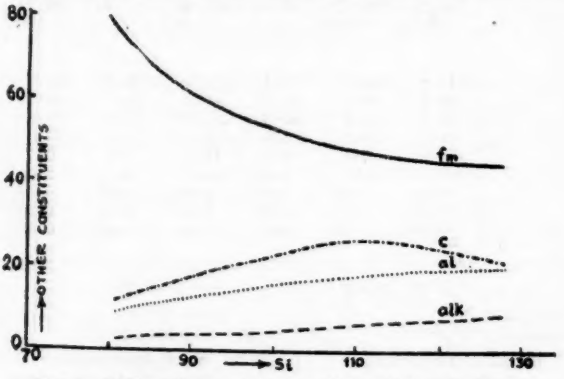


FIG. 3 Differentiation diagram of the Cuddapah Traps

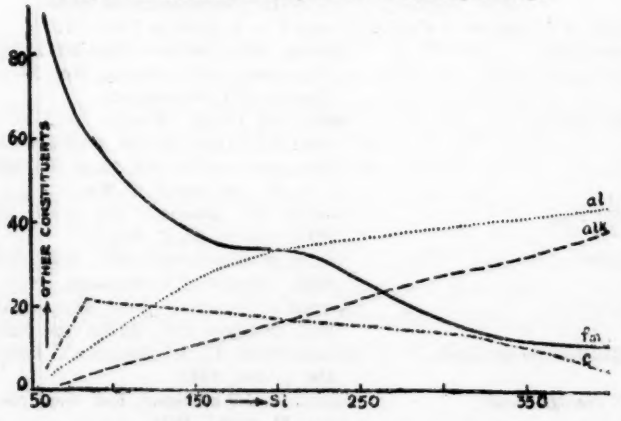


FIG. 3*a*. Differentiation diagram of the calc-alkali series (After Niggli)

constituents as ordinate. There are three curves which are roughly mutually sympathetic, but antipathetic to the *fm* curve. The curve *c* rises more rapidly than the *al* curve but it becomes sympathetic to *fm* curve at about *si* 112. The *alk* curve, on the other hand, rises only very gently. The *fm* curve is steep from *si* 81 to 110, the value of *fm* changing rapidly for a small variation in *si*, but it becomes flatter afterwards.

The Niggli differentiation diagram does not give us an idea of the individual behaviour of soda and potash, or of magnesia which are grouped together in the *alk* and *fm* values. To study this, the values *k* and *mg* can be plotted, with *k* as abscissa and *mg* as ordinate. The relationship between these two components during the progress of differentiation can be understood from Fig. 4. It is seen that there is comparatively little variation in *k*,

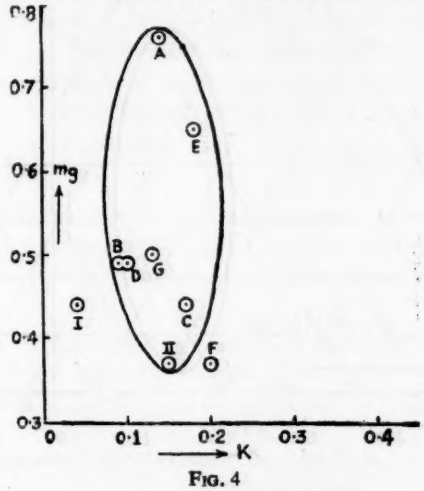


FIG. 4

k—*mg* diagram for the Cuddapah Traps

the maximum being 0·16, while the *mg* values have a range of as much as 0·39. The points occupy a small linear zone which is nearly vertical in position to the abscissa, this being found commonly in potash suites. The reciprocal relationship which is characteristic of calc-alkaline suite is not clearly seen in the diagram.

The normative mineral composition of a rock can be estimated from its Niggli values. When there is enough silica and when *al* is less than the sum (*alk* + *c*), the value 2 *alk* gives the proportion of the alkali-feldspars, 2(*al* − *alk*) that of the anorthite content, and (100 − 2 *al*) that of the melanocratic (ferromagnesian) minerals. The sum of these three values is

always equal to 100 and can be represented by a single point in a trilinear co-ordinate diagram in which the three corners represent 100 per cent. of the three values.

When these values are plotted on a trilinear co-ordinate diagram (Fig. 5), a clear idea is gained of the basicity of the rocks and also of the general trend

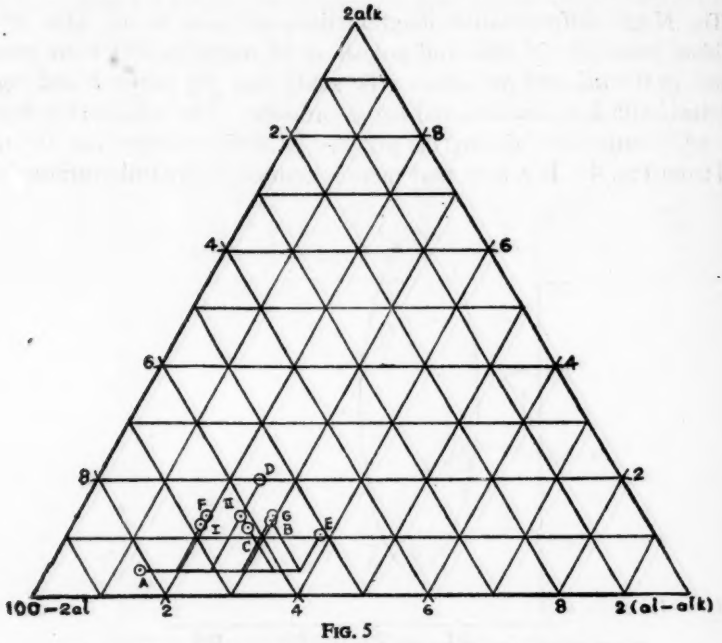


FIG. 5

2 *alk* − 100 — 2 *al* − 2 (*al* − *alk*) diagram for the Cuddapah Traps

of consolidation of the magma, which conforms to the theory of crystallisation-differentiation, *viz.*, the progressive enrichment in alkali feldspar.

From the diagram the magma can be regarded as having followed three different lines of development during the evolution of the various types.

1. The impoverishment in ferromagnesians with constant alkali-feldspars.
2. The enrichment in alkali-feldspars with constant dark minerals.
3. The enrichment in alkali-feldspars with constant anorthite content.

From the point A the first trend operated and, during the progress of this, the second and third courses have given rise to the other types. We cannot say definitely which type is the result of these two differentiation

tendencies as the points can be joined either way, but we can regard the types E and D as resulting from the enrichment of alkali-feldspars with constant anorthite content. Of these two, the type D has higher alkali-feldspars while E is richer in anorthite content.

The QLM-Diagram

The *QLM*-diagram is very important in tracing the magmatic affinities of the rocks and the sequence of formation of the various types and also the order of crystallisation of the minerals composing the rocks. As the role of quartz is important in the formation of different rocks, the behaviour of quartz in the differentiation history can very well be followed in this diagram.

When the *QLM* values (Table V) of the Cuddapah magma types are plotted in the diagram (Fig. 6) prepared by Niggli (1938, Figs. 2*a*, 20 and 21), it is seen that all the points except A fall below the line PF (saturation line) and above PL in the area of ' Normal basalt ' within the main basalt field. The point A, representing a peridotitic type falls outside the above field. All the so-called ' primary basalts ' of all parts of the world (such as tholeiite, ophiolith, norite, plateau-basalt and olivine-basalt) fall within the borders of ' Normal basalt '.

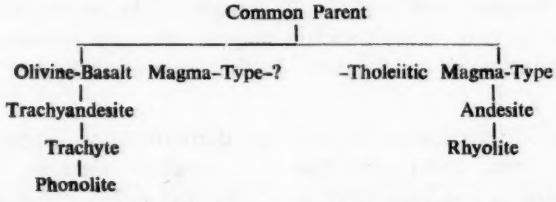
Most petrologists now regard all igneous rocks as derived generally from a basaltic magma, though such a magma may not necessarily be considered the starting point in all cases. In this connection Bowen has written (p. 5, 1928):

> " To Daly, in particular, we owe the demonstration, apparently satisfactory, that basaltic magma is a constant member of all these associations and that there is no essential difference in the basaltic magma of the various associations. Partly for this reason and partly on geologic grounds he considers that basaltic magma is the parental magma of all igneous-rock series, except certain pre-Cambrian rocks. The facts are not such as to enforce belief in the parental nature of basaltic magma but they are sufficiently definite that many petrologists now entertain the belief favourably and include it in their general scheme of rock derivation. In the present discussion the parental nature of basaltic magma is taken as a fundamental thesis and other rock-types are developed principally by fractional crystallisation..... The reasons for preferring a thoroughly basic, presumably basaltic, parental magma are, however, strong and will become apparent as the discussion proceeds."

Thus Bowen derives the various rock types from basic and basaltic magma, supported by his experiments on liquid melts in the laboratory.

To him crystal fractionation is the chief cause of the diversity of rocks. He believes that basaltic magma generally gives rise to quartzose late differentiates but under certain conditions a liquid deficient in silica may be filter-pressed before reaction with early-formed crystals such as pyroxenes; or the liquid may be rich in silica if filter-pressed during peritectic reaction, leaving behind feldspathoids. Daly, on the other hand, considers that 'primary basalt' magma is capable of giving rise to various rock-types but he attributes the formation of alkaline rocks primarily to the desilication of basaltic magma by wide-spread assimilation of limestones and calcareous sediments. Thus both the authorities view the alkaline rocks as abnormal and derived under exceptional circumstances from the 'primary basaltic' magma. Contrary to the views of Bowen and Daly, W. Q. Kennedy (p. 256, 1933) basing his conclusions on the investigations of the authors of the Mull Memoir, says:

> "Study of individual rock bodies and regional magmatic provinces leads to the conclusion that there exist two great primary basalt magmas, the olivine-basalt type and the tholeiitic basalt type, each of which gives rise normally to its own particular line of descent. The former is the parent of the alkaline rock suite and the latter is the parent of the calc-alkaline suite as follows:



> There is no evidence that either of these "primary" magmas is a derivative of the other nor can we point to any common parent from which they could have been derived....." "Any such relationship is too far removed from the scope of the present investigation to merit discussion, and all that seems certain is that both types of basaltic magma have been available throughout geological history in immense amounts and over immense areas. We are justified, therefore, in regarding them, for the purposes of petrogenesis, as primary magmas."

Thus Kennedy maintains that a particular late differentiate is determined only by the nature of the primary magma and is not the result of the physico-chemical conditions obtained during solidification.

Niggli (1938) prefers to assume two or even a larger (yet limited) number of well-defined basaltic 'Stammagmas' ("Zwei oder einer kleinen Zahl

wohldefinierter basaltischer Stammagmen," p. 653, 1938) for the derivation of rock-types of petrographic provinces. Niggli uses the terms 'Ausgangs' or 'Stammagma' instead of 'primary magma' since there is a great variation in the composition of the basic magma, as is shown by the large basaltic field in the *QLM*-diagram (Fig. 6).

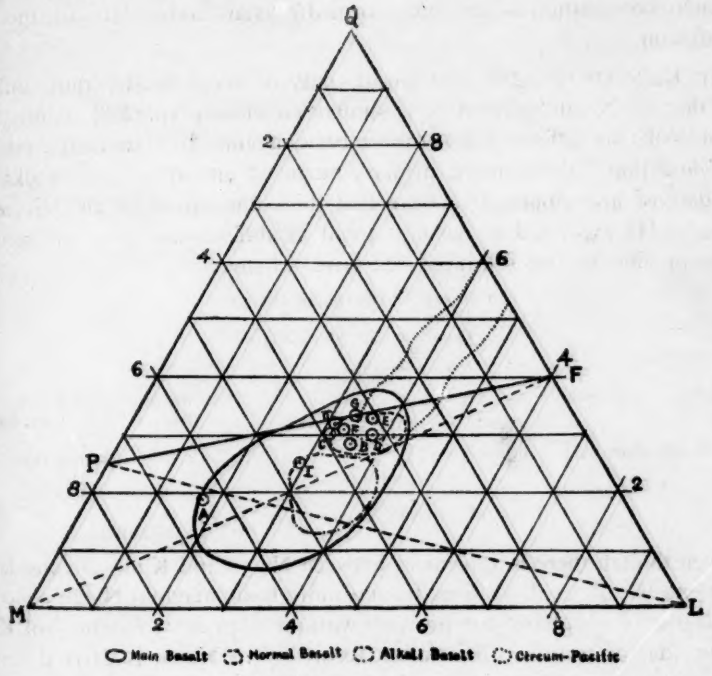
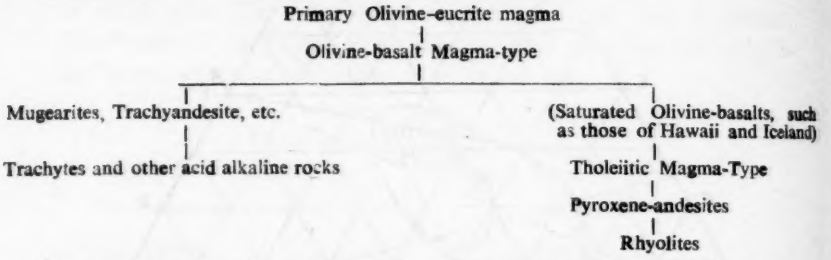


FIG. 6
QLM – Diagram of the Cuddapah Traps

Basing his observations on his molecular values, Niggli has found that the olivine-basalt or 'plateau-basalt' type is essentially of normalgabbroid to hornblenditisch and that the tholeiitic type varies from normalgabbrodioritisch to miharaitisch. He says that the theory of Kennedy holds often, but on a careful investigation one can observe all possible intermediate members in between these two types; as the chemical difference itself is relatively small, so that normalgabbroid types are found also in typical Pacific provinces and gabbrodioritisch in the Atlantic. On a comparison of the molecular values of tholeiite and norite and of 'plateau-basalts' and tholeiites, and from the association of hornblenditisch and hornblendeperidotitisch

types with 'plateau-basalts' and tholeiites, he concludes that tholeiite was derived from completely fluid magmas of hornblenditisch and hornblende-peridotitisch composition and that, as these magmas give rise to heteromorphous rock-types with such monomineralic rocks as amphibole picrite and hornblendite which exhibit similar composition included in them, the further course of differentiation depends entirely upon the predetermined primary molecular constitution of the early formed crystals combined with the trend of diffusion.

H. Kuno (1937), after a chemical study of many basalts, quite different from that of Niggli, arrived at a similar conclusion (p. 208), namely, that "these rocks are differentiates of more basic magmas by fractional crystallisation" and that "the ultimate primary magma from which these rocks have been derived are supposed to have had the composition of an olivine-rich eucrite." He expressed the general trend of differentiation of this primary eucrite magma in the following tentative scheme:



Even though there is agreement between Niggli and Kuno in considering the plateau-basalts as derivatives from a more basic magma, Niggli conceives of a magma of ultrabasic composition while the 'primary magma' of Kuno is gabbroidal or noritic. This latter according to Niggli is derived from a more basic magma; but the attractiveness of Kuno's theory lies in considering the tholeiite type as the derivative of olivine-basalt which is an amplification of the observations of Niggli.

In conceiving of the plateau and olivine-basalt magmas as derived from liquid ultra-mafics, we have to face the objection raised by Bowen. Bowen (1927 and 1928) denies the existence of peridotitic magma and concludes that monomineralic rocks such as dunite, anorthosite, etc., do not represent the composition of the magma from which they were formed but are accumulations of early-formed crystals which separated from the liquid by crystal fractionation. He supports his view by experimental work on liquid melts which indicates that ultra-mafic magmas can be liquid only at prohibitively high temperatures. But C. N. Fenner (1938) and H. H. Hess (1938) consider

that hyperfusible constituents would have a controlling effect on the temperature. C. N. Fenner states (p. 399, 1938):

> "This leads to the conclusion that, contrary to inferences reached in the theory of crystal fractionation, wholly liquid magmas of ultrabasic composition exist."

The views of Fenner and Hess may perhaps be verified in a few localities, but it may not follow that all peridotites represent direct product of solidification from the magma of the same composition. On the other hand, Bowen has clearly shown that certain peridotites are the result of accumulations of early-formed crystals from a basaltic or noritic magma. In the case of the peridotites of Skye he pointed out that the chilled marginal facies of the ultra-mafics carried phenocrysts of olivine in a fine-grained basaltic matrix, indicating that the core is the result of accumulations of early crystals from which the residual liquid was filter-pressed. We should, therefore, look for positive proof in the field regarding the origin of such types as the trap from which the (analysed) specimen A was collected. In this connection it may be worth noting that C. S. Fox (quoted by A. L. Coulson, p. 150, 1934) describing the occurrence and field relations of this trap, states:

> "The ridge (west of Pulivendla Inspection Bungalow) appears to consist of a composite sill (three separate sills) of dolerite, the middle one, a dark, coarse, scoriaceous-weathering rock being rich in olivine, while the layers above and below it are dolerites without olivine."

A. L. Coulson comments thus on the statement of Fox:

> "These observations of Dr. Fox have great interest and deserve amplification. The author collected specimens of the sill which bear out Dr. Fox's remarks. Thus the uppermost part of the sill is best described as a quartz-dolerite. It is very similar to a specimen of what is undoubtedly the same sill collected near the 38th milepost on the Cuddapah-Pulivendla road, 1¼ miles WNW of Vemula."
>
> "The central portion of the sill is very basic and contains abundant augite, olivine, (?) hypersthene, serpentine, a little feldspar, iron-ore and brown mica. It is a picrite. It also has its counterpart in a similar specimen collected near Vemula.
>
> The lowest portion of the compound sill is intermediate in basicity between the uppermost and central parts, being best described as a dolerite."

From his own field and laboratory studies the present writer is quite in agreement with the above description. The upper and lower dolerites do

not appear to be the border facies formed as the result of filter pressing of the residual liquid, nor do they contain any olivine phenocrysts to warrant such an assumption; but they do represent quite separate phases of intrusion. It is suggested, therefore, that type A represents the primary magma of the composition of picrite from which other types were possibly differentiated.

In Fig. 6 is shown the main basalt field in which are distinguished 'Normal basalt' and 'alkali basalt' and a well marked area of calc-alkaline rocks. It can be seen that the major portion of the 'Normal basalt' represented by tholeiite, ophiolith and 'plateau-basalt' is occupied by calc-alkaline field. When the *QLM* values of the Cuddapah traps are plotted, it is seen that all the normal types occupy the region of 'Normal basalt' while A and I which are distinctly earlier in the differentiation series are found towards the side M. There is only one trend of differentiation, from picritic composition towards the calc-alkaline field as shown below:

Picrite (hornblendeperidotitisch)
(*si*-pyroxenitisch
dolerites normalgabbroid or *c*-gabbroid)
quartz dolerites (normalgabbrodioritisch or miharaitisch)

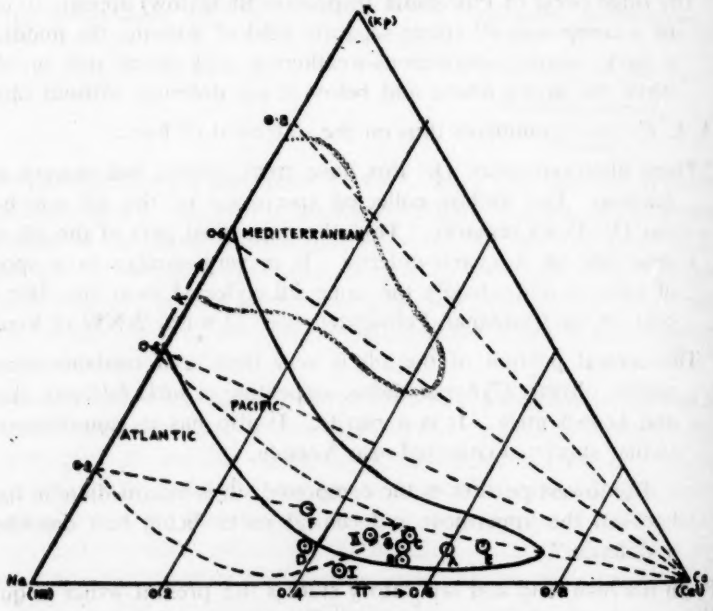


FIG. 7
k_m Diagram for the Cuddapah Traps

The kπ-Diagram

The same trend of differentiation is also indicated when we study the interrelation between the three Basis molecules Kp, Ne and Cal, which is brought about by k and π values themselves, on a triangular diagram whose corners are Kp, Ne and Cal, in which the three generalised diagrams constructed by Niggli (Figs. 2*b*, 3*b* and 4*b*, 1938) for the three petrographic suites are included in a simplified form. When k and π values for the Cuddapah traps are plotted in the diagram (Fig. 7) it is seen that except for the points D and I all the others fall within the field of the Pacific suite.

It is evident from these studies that the Cuddapah intrusive belongs to the calc-alkaline suite.

Summary and Conclusion

The traps of Cuddapah age mark an important period of volcanic activity later in age than the Dharwars and probably earlier than the Cambrian. The chief character that distinguishes the Cuddapah traps from those of Dharwar age is the marked freedom of the former from metamorphism as the Peninsula was free from major earth movements after their intrusion.

In the present work an attempt is made to study the petrography and petrochemistry of these basic rocks collected from several sills intrusive into the Vempalle limestones and the Tadpatri shales in the Ceded districts.

These trap rocks are composed of colourless, non-pleochroic pyroxenes and labradorite feldspars with sub-ophitic to doleritic textural relationship between these two minerals indicating that they crystallised more or less simultaneously. This is also confirmed by the f(norm) values. The pyroxenes belong mostly to the monoclinic variety, augite, the other monoclinic pyroxene, pigeonite being rare or absent; in the olivine-bearing types there is also the rhombic pyroxene, enstatite. The optic axial angle of the augite varies from 56° to 40° and the extinction angle from 46° to 36°. The enstatite is optically negative ($2V = -83° \pm 2°$) and is rich in magnesium.

The Cuddapah traps, the Newer dolerites and the Gwalior traps are similar to each other in their pyroxenes being mainly augite with a large optic axial angle. They differ from the Deccan traps, the Karroo dolerites, the Whin Sill and the New Jersey diabases in the absence of pigeonite which characterises those rocks. The average composition of the plagioclase, deduced from both Universal Stage determinations and chemical analyses is found to range from bytownite with 75 per cent. anorthite to oligoclase or andesine of 30 per cent. anorthite with a mean value of about 55 per cent. anorthite.

From a study of the analyses, six distinct magma-types (Niggli's) have been recognised:

1. Melagabbrodioritisch
2. Miharaitisch
3. Normalgabbroid
4. *c*-gabbroid
5. *si*-pyroxenitisch
6. Hornblendeperidotitisch.

Petrochemical studies, using Prof. Niggli's methods, show that the rocks are basaltic in nature with only a limited range of differentiation. The differentiation diagram based on the Niggli molecular values, ***QLM*** values and $k\pi$ values show that the Cuddapah magma belongs to the 'Normal basalt' of Niggli (= Tholeiite type) and that the trend of differentiation is similar to that of the calc-alkaline suite of rocks.

These conclusions are only of a limited validity as the number of specimens analysed is small. As these traps occur extensively and over large areas, there is scope for the extensive collection and study of much material which will lead to a wider understanding of the nature and history of these rocks.

ACKNOWLEDGEMENTS

In conclusion, I wish to express my gratefulness to Prof. T. N. Muthuswami, Professor of Geology, Presidency College, Madras, for guidance during the whole course of this work and for giving me all facilities for laboratory work. I am indebted to Mr. M. S. Balasundaram, Assistant Geologist, Geological Survey of India, for affording me an opportunity of studying some of his collections of Cuddapah traps from the Ceded districts for purposes of comparison. Lastly, I wish to place on record my sincere thanks to Dr. M. S. Krishnan of the Geological Survey of India for many useful and instructive suggestions in the presentation of the results of this study.

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CHEMICAL EXAMINATION OF THE FRUITS OF *TERMINALIA BELERICA* ROXB.

Part II. The Component Clycerides of the Fatty Oil

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Received April 12, 1946

[The component glycerides of the seed oil of *Terminalia belerica* have been examined. The amounts of oleic, linoleic, palmitic and stearic acids have been found to be in fair agreement with those reported[1] in Part I. The component glycerides of the oil are Palmitooleolinolein 35·24%, Stearooleolinolein 43·51%, Palmitodiolein 1·07%, Stearodiolein 1·95%, Dioleolinolein 9·54% and Triolein 8·69%.]

In a previous communication,[1] the percentage composition of the component fatty acids of the oil from the kernels of the fruit of *Terminalia belerica* (natural order *Combretaceæ*) has been reported by Saran and Singh; the present work is in continuation of it and deals with the glyceride structure of the oil. A few other species of *Terminalia* have also been examined for the composition of seed oil, namely, *T. catappa* from East Indies[2] and West Africa[3] and *T. chebula*.[4] The major component acids of these oils are oleic, linoleic and palmitic, stearic acid being present in only minor proportions. The fatty acid composition of *T. belerica* as found directly by Saran and Singh is in fair agreement with that determined from the glyceride composition of the oil as shown below:

	Oleic	Linoleic	Palmitic	Stearic
Saran and Singh (direct determination) ..	43·21%	28·99%	11·80%	16·00%
Present authors (glyceride structure) ..	43·68%	29·56%	11·28%	15·48%

It will be thus seen that oleic and linoleic acids are the major components of all *Terminalia* species, the amount ranging between 56 to 84%. There is, however, this difference that whereas stearic acid is present only in minor proportions and is not a major component in other species of *Terminalia* so far investigated, it becomes a major component (over 15%) along with palmitic acid (over 11%) in the seed oil of *T. belerica*.

The number of glycerides present in the seed oil of *T. belerica* is found to be six, whereas the total number of glycerides which can be formed from four acids and the glyceryl radical, $CH_2-CH-CH_2$, is forty.

Experimental

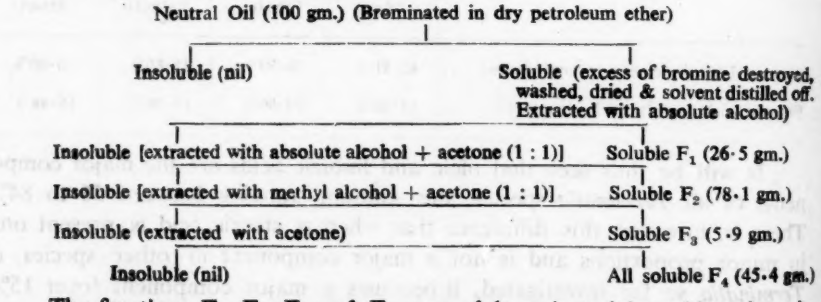
The oil extracted from the crushed kernels of the fruit of *T. belerica* with petroleum ether (40°–60°) was purified with animal charcoal and Fuller's earth, dried over fused calcium chloride, neutralised with sodium carbonate and filtered.

One hundred grams of the oil was chilled[5,6] in the frigidaire with six times its weight of pure and dry acetone for a week. No solid separated showing the absence of trisaturated and disaturated-monounsaturated glycerides. The experiment was repeated twice with each of the following samples of the oil:—

(*a*) Freshly extracted and purified oil, (*b*) about one year old oil, and (*c*) sample of oil used by Saran and Singh, but in no case any solid glyceride separated. The absence of trisaturated glyceride was further confirmed by oxidising the oil dissolved in pure and dry acetone with powdered potassium permanganate.[7]

One hundred grams of the oil was brominated[8,9] in ten times its weight of dry petroleum ether (40°–60°) at − 5° C. till the brown colour persisted. It was kept in the frigidaire overnight. No solid separated. Excess of bromine was destroyed with sodium thiosulphate solution, washed, dried over fused calcium chloride and the solvent distilled off. The viscous residue was extracted with absolute alcohol, absolute alcohol + acetone (1 : 1), methyl alcohol + acetone (1 : 1) and acetone in succession.

The scheme of separation is given below:—


Neutral Oil (100 gm.) (Brominated in dry petroleum ether)
Insoluble (nil)
Soluble (excess of bromine destroyed, washed, dried & solvent distilled off. Extracted with absolute alcohol)
Insoluble [extracted with absolute alcohol + acetone (1 : 1)]
Soluble F1 (26·5 gm.)
Insoluble [extracted with methyl alcohol + acetone (1 : 1)]
Soluble F2 (78·1 gm.)
Insoluble (extracted with acetone)
Soluble F3 (5·9 gm.)
Insoluble (nil)
All soluble F4 (45·4 gm.)

The fractions F_1, F_2, F_3 and F_4 were debrominated by taking them in methyl alcohol, adding zinc dust, saturating with dry hydrogen chloride gas

and heating for several hours under reflux in the water-bath. The brominated products were saponified, the unsaponifiable matter removed and the mixed fatty acids liberated. The quantity of individual acids in each fraction was estimated by determining their saponification equivalent and iodine and thiocyanogen values. The quantities of saturated acids being too small in these fractions for estimating them separately, they were considered as one acid and their mean molecular weight determined on extracting with petroleum ether (40°–60°), the oxidation products of each fraction with alkaline potassium permanganate.[10] The glyceride structure was calculated with these data as given below in Tables I to VI.

TABLE I

	F_1	F_2	F_3	F_4
Weight of Brominated glyceride in grams ..	26·5	78·1	5·9	45·4
" Unsaponifiable matter in gm. ..	·25	·26	·002	·011
" Debrominated glyceride in gm. ..	17·52	49·82	3·72	28·95
" " " free from unsaponifiable matter	17·27	49·56	3·72	28·94
Weight % of acid ..	17·36	49·80	3·74	29·10
Mol. % of acids ..	17·24	50·13	3·73	28·90
Iodine value of liberated acids ..	84·98	93·09	97·45	96·58
Thiocyanogen value of liberated acids ..	59·94	64·03	67·84	73·00
Mean molecular weight of " " ..	276·5	272·7	275·1	276·7
Mean molecular weight of solid acids ..	275·0	270·4	273·9	275·4

TABLE II. *Weight % of acids in different fractions*

	F_1	F_2	F_3	F_4
Linoleic ..	27·64	32·07	32·68	26·03
Oleic ..	38·81	38·89	42·51	54·95
Solid ..	33·55	29·04	24·81	19·02

TABLE III. *Weight % of acids on total acids*

	F_1	F_2	F_3	F_4	Mean
	17·36	49·80	3·74	29·10	100
Linoleic ..	4·80	15·96	1·22	7·58	29·56
Oleic ..	6·74	19·36	1·59	15·99	43·68
Solid ..	5·82	14·48	0·93	5·53	26·76

TABLE IV. *Mol. % of acids in different fractions*

	F_1	F_2	F_3	F_4
Linoleic ..	27·53	31·81	32·58	26·04
Oleic ..	38·30	38·32	42·09	54·64
Solid ..	34·08	29·87	25·33	19·36

TABLE V. *Mol. % of acids on total acids*

	F_1	F_2	F_3	F_4	Mean
	17·24	50·13	3·73	28·90	100
Linoleic ..	4·74	15·95	1·21	7·53	29·43
Oleic ..	6·62	19·21	1·57	15·78	43·18
Solid ..	5·88	14·97	0·95	5·59	27·39

TABLE VI. *Probable glyceride structure*

	F_1	F_2	F_3	F_4	Mean
	17·24	50·13	3·73	28·90	100
1 Trisaturated glyceride ..	Nil	Nil	Nil	Nil	
2 Disaturated monounsaturated ..	,,	,,	,,	,,	
3 Monosaturated diunsaturated—					
(*a*) , oleolinolein ..	14·22	44·91	2·85	16·77	78·75
(*b*) ,, diolein ..	3·02	3·02	..	..	3·02
Triunsaturated—					
(*a*) Dioleolinolein ..	..	2·94	0·78	5·82	9·54
(*b*) Triolein ..	..	2·28	0·10	6·31	8·69

1. By oxidizing the neutral oil dissolved in pure and dry acetone with powdered potassium permanganate.

2. By chilling the neutral oil dissolved in pure and dry acetone at 0° C.

3 & 4. By calculating from the component fatty acids of the brominated glyceride in the oil.

All the saturated acids have been considered as one acid in the calculation of monosaturated-diunsaturated glycerides. According to the law of even distribution we are justified in assuming that the greater proportion of glycerides exist as monosaturated oleolinolein rather than monosaturated diolein and monosaturated-dilinolein. Further it has been assumed that the solid acids are proportionally divided in different glycerides. From the

above considerations the probable glyceride structure may be given as: Palmitooleolinolein 35·24%, Stearooleolinolein 43·51%; Palmitodiolein 1·07, Stearodiolein 1·95%, Dioleolinolein 9·54% and Triolein 8·69%.

Acknowledgement

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